Methods for characterizing defects on silicon surfaces, etching composition for silicon surfaces and process of treating silicon surfaces with the etching composition

The present invention relates to a method for characterizing defects on silicon surfaces, in particular silicon wafers, a method for treating silicon surfaces with an etching solution and the etching solution to be employed in the method and process of the present invention.

Prior art

Crystalline defects in substrate for microelectronic devices are highly undesirable as they have a negative impact on the functionality and reliability of integrated circuits, formed using the substrates, such as wafers, in particular silicon-on-insulator (SOI) type wafers. The typical approach for identifying crystalline defects and thereby characterizing the quality of substrate surfaces is the use of so-called structural etching solutions. These etching solutions, due to the dependency of the etch rate from crystalline structures, can identify crystalline defects, since crystalline defects give rise to either hillocks or etch pits after application of the structural etching solution.

Various etching solutions have been proposed for silicon surfaces which require typically the presence of strong oxidants.

F. Secco describes in Journal of Electrochemical Society, 119, no. 7, pp. 948-951 (1972) an etching solution for revealing etch pits in silicon, consisting of a mixture of hydrofluoric acid and aqueous alkali dichromate. The alkali chromate acts as oxidizing agent while the hydrofluoric acid dissolves the oxidation product, namely silicon dioxide. However, chromates and, in particular, dichromates are highly toxic due to their ability to interact with cells and DNA.

W.C. Dash in the Journal of Applied Physics, vol. 27, no. 10, pp. 1193-1195 (1956) discloses a further etched solution able to reveal defects on semiconductor substrates, consisting of hydrofluoric acid, nitric acid and acetic acid. While this solution is able to etch semiconductor substrates, including silicon substrates, the etching solution

according to Dash is not able to differentiate between different types of defects and furthermore does not provide a satisfactory etch rate.

US 2,619,414 discloses a further chemical etchant to be applied on semiconductor surfaces to improve their electrical characteristics. The chemical etchant disclosed in US 2,619,414 comprises acetic acid, nitric acid, hydrofluoric acid and bromine. The drawback of the composition as disclosed in US 2,619,414 is the use of bromine, which is highly instable and volatile, so that the chemical etchant according to this prior art reference can only be stored for a very short time in the dark at low temperatures and can be handled only under ventilation, since bromine evaporates from the composition. Although bromine is not as toxic as chromate or dichromate, precautionary measures nevertheless have to be taken when using the chemical etchant according to US 2,619,414.

Objects of the present invention

In view of the progress in semiconductor industry, involving in particular the decrease of the minimum feature sizes used to fabricate integrated circuits, the introduction of new substrate materials, such as silicon-on-insulator (SOI) or strained-silicon-on-insulator (sSOI), improved methods for quality characterization are required, in particular with respect to the following features:

- Satisfactory etch rates, so that even thin substrates can be etched with a sufficient control of etch rate/etch time/removed surface thickness.

- Etch sensitivity, i.e. the possibility to detect different types of defects (such as D defects corresponding to agglomerates of vacancies and oxygen precipitates), most preferably identifying different types of defects after one type of etching treatment.

- Reduction of health risks and environmental problems by using suitable components for the etching composition, without sacrificing the desired properties, etch rate, etch sensitivity etc.

- Stability of the etching composition, so that same can be stored for a certain period of time and can be handled without highly elaborated safety measures.

Brief description of the invention

The above-outlined object has been solved with an etching solution as defined in claim 1. Preferred embodiments are defined in subclaims 2 to 5. The present invention furthermore provides a method for characterizing defects on silicon surfaces as defined in claim 6. Preferred embodiments thereof are defined in subclaims 7 to 10 and 15.

Finally, the present invention provides a process for etching silicon surfaces as defined in claim 11. Preferred embodiments are defined in subclaims 12 to 15. Further preferred embodiments are also explained in the following description.

Brief description of the figures

Figure 1 shows a graph displaying the dependency of the etch rate as a function of the content of acetic acid. Figure 2 shows a graph showing a correlation between etch rate, acetic acid content and etch pit density.

Figure 3 displays a graph showing the correlation between etch rate and concentration of hydrofluoric acid. Figure 4 shows the influence of Br_2 content on etch rates while Figure 5 shows the influence of nitric acid on material consumption and so its necessity for etch pits delineation. Figure 6 represents a comparison of etch pit densities as obtained with etching compositions in accordance with the present invention, compared with a composition in accordance with the prior art reference Secco. Figures 7 and 8 likewise display a similar comparison, employing etching compositions in accordance with the present invention which had been stored for several days. Figure 9 shows the evolution of the etch rate with decreased temperature (down to 8°C). Figure 10 plots the comparison of EPD (Etch Pits Densities) with etching composition in accordance with the present invention from room temperature down to 8°C, compared to the Secco reference.

In the Figures etching solutions in accordance with the present invention are also designated Crless SOI x/y/z, with x/y/z indicating the molar ratio HF/HNO_3/acetic acid.

Detailed description of the present invention

The present invention will be first described in connection with the etching solution. The preferred embodiments discussed herebelow however also apply with respect to the methods of the present invention, unless otherwise stated.

The present invention is mainly characterized in that a novel etching solution for treating semiconductor surfaces is provided. The etching solution in accordance with the present invention comprises hydrofluoric acid, nitric acid, acetic acid, an alkali bromide and an alkali bromate, preferably sodium bromide and sodium bromate. The components of the etching solution in accordance with the present invention are explained in further detail below:

1.) The hydrofluoric acid to be employed in accordance with the present invention preferably is an aqueous solution of HF with a concentration of above 30%, preferably above 40%, more preferably above 45%, such as about 49%.

2.) Furthermore, the etching solution in accordance with the present invention comprises nitric acid. The nitric acid to be employed in accordance with the present invention again preferably is an aqueous solution, typically showing a nitric acid concentration of above 50%, more preferably above 60%, and in particular above 65%, such as about 70%.

3.) The acetic acid to be employed in accordance with the present invention preferably is a pure acetic acid, such as an acetic acid commercially available as glacial acetic acid having an acetic acid content of 99%.

4.) The alkali bromide and the alkali bromate are preferably sodium bromide and sodium bromate respectively, although also other alkali salts, such as potassium salts may be employed.

Preferably the etching solution in accordance with the present invention consists of the components identified above, i.e. the etching solution is an aqueous mixture, preferably solution, of the components mentioned above.

These components of the etching solution in accordance with the present invention may be present in the overall mixture in the following amounts:

Acetic acid: 20 to 90 vol%, based on the overall composition of the etching solution , preferably 30 to 90 vol%, more preferably 50 to 90 vol%, calculated on the basis of an acetic acid having a concentration of 99%.

Hydrofluoric acid: 2 to 30 vol%, preferably 10 to 25 vol%, more preferably 15 to 25 vol%, calculated on the basis of an aqueous HF having a concentration of 49%.

Nitric acid: addition amounts so that the molar ratio HF/HNO_3 is from 1:2 to 1:15, preferably 1:2 to 1:10, more preferably 1:5 to 1:8, in particular 1:7.5

Ratio HF/CH_3COOH: preferably adjusted to a molar ratio of from 1:5 to 1:15, preferably 1:7 to 1:10, in particular 1:7.9

Alkali bromite and alkali bromate: ratio of bromate to bromide of 1:5, so that a molar bromine concentration, resulting from the reaction of bromate and bromide according to the equation $NaBrO_3 + 5NaBr + 6H^+ = 3Br_2 + 3H_2O + 6Na^+$, amounts to from 0.02 to 0.5, preferably 0.04 to 0.3, more preferably 0.048 to 0.288.

The etching solution in accordance with the present invention may be prepared by simply mixing the components identified above in the desired ratio, typically using conventional safety measures. The order of addition of the components is not critical and the components usually are mixed within a stirred vessel. The composition as obtained may be stored without loss of etching activity for several days, typically under cooling conditions.

The use of an etching solution in accordance with the above is highly satisfactory. The etching solution as defined above provides for an etch rate which is low enough so that even thin semiconductor substrates can be etched, without sacrificing the desired etching properties, such as formation of well developed etch pits, facilitating the surface

characterization. Due to the relative high acetic acid content in the preferred etching solution in accordance with the present invention, highly satisfactory homogeneous surfaces can be obtained and the use of bromate and bromide alleviates the necessity to employ bromine as starting ingredient.

With an etching solution in accordance with the present invention, it is possible to reveal surface defects on semiconductor substrates, even on thin substrates, such as SOI or sSOI substrates. The shape of revealed etch pits are mainly conic shallow pits and observable as round mark (spot) after etching treatment (see figure 9). The etching solution in accordance with the present invention, depending from the actual composition, provides etch rates of 3 to 70 Å/sec, so that highly satisfactory total etch times can be achieved even when using thin substrates, such as SOI substrates where it is required to remove about 500 to 600 Å of the initial surface.

In this respect, it furthermore has been shown, using the etching solution in accordance with Secco (see above) as reference, that the solution in accordance with the present invention enables a highly satisfactory and reliable identification of defects, as evidenced by the very similar etch pit densities obtained. These experiments furthermore show that the etching solution in accordance with the present invention even may be stored for at least up to 3 days at room temperature without sacrificing the etch properties (see figures 4 to 8).

Overall, it is therefore readily apparent that the etching solution in accordance with the present invention enables a vast improvement compared with the etching compositions as known so far from the prior art.

Preferred embodiments in accordance with the present invention are further illustrated by the Figures, discussed below.

Figure 1 shows that the etch rate in particular can be controlled by adjusting the acetic acid content. Higher etch rates are obtained with low acetic acid contents. Too high contents of acetic acid however also may be detrimental in that delamination could be induced. Figure 2 further shows that too high contents of acetic acid also may be detrimental in that fewer defects are identified, as evidenced by the lower EPD values. Figure 2 shows also that the ratio HF/HNO_3 may be adjusted in accordance to the low etch rate and enables at the same time the formation of etch pits. In particular, a ratio

HF/HNO_3 1/7.5 is preferred to keep a good compromise between etching and defects delineation. Figure 3 shows that etch rates may also be adjusted by adjusting the HF content. Higher HF contents usually give rise to higher etch rates. Figure 4 shows that also the molar Br_2 concentration, resulting from the reaction of bromide and bromate, enables a control of the etch rate. Figure 5 displays that the nitric acid is needed for the surface oxidation and that the content has to be adjusted to enable a control of the etch rate and the etch sensitivity (ratio preferred HF/HNO_3 > ½). No etch pits could be detected without nitric acid, confirming that the capability for making defects visible is lead back to the presence of nitric acid.

Figures 6 to 8 show that the etching solution in accordance with the present invention reveals very similar EPD, compared with the standard Secco composition, even after storage for 1 to 3 days, a storage not possible with the composition disclosed in US 2,619,414.

Figure 9 shows that the etch rate of the solution can also be controlled by decreasing the temperature of the mixed solution. This cooled etch solution can then typically be applied for etching of thin SOI surfaces (from 0 to 800 Å), enlarging the range of potential substrates.

Figure 10 shows that the etching composition in accordance with the present invention reveals very similar EPD even at lower temperature than the room temperature (from 23°C to 8°C), compared with the standard Secco composition. Decreasing the temperature of the solution for thin film application does not influence the EPD.

The experiments as illustrated in Figures 9 and 10 show one further important aspect in accordance with the present invention. Without sacrificing the EPD, the reliability of the etching process, the etching solution in accordance with the present invention may be employed at rather low temperatures with highly efficient etching results, so that a further control of the etching process is enabled. Due to the rather low etching rates at low temperature, it is in particular possible to etch, with a sufficiently high degree of control, very thin substrates without endangering the overall integrity of the substrate to be treated.

It is accordingly possible to conduct etching over a wide range of temperatures, such as from 5 to 50°C, preferably 5 to 25°C, and depending from the circumstances either at

low temperatures such as from 5 or 8 to 15°C, or at higher temperatures, such as from 20 to 25°C, in embodiments 23°C.

Further, as already outlined above, the present invention provides a method for characterizing defects on silicon surfaces as well as a process for etching silicon surfaces, which both comprise a step of etching a silicon surface with an etching solution as defined herein.

In the method as well as the process in accordance with the present invention the silicon surfaces may be surfaces of semiconductor substrates, such as conventional silicon substrates or preferably SOI or sSOI materials.

These substrates may be subjected to any conventional pretreatment, and after application of the etching solution in accordance with the present invention, the substrates again may be subjected to conventional post-treatments such as washing, drying etc. as required.

As indicated above, the use of the etching solution in accordance with the present invention enables a superior control of the etch rate together with highly satisfactory etch results, i.e. highly reliable detection of defects on the treated surface.

The present invention accordingly proves that it is possible to use the etching solution that has been described in an industrial etching process in replacement of the reference Secco solution.

Claims

1. Etching solution, comprising HF, HNO_3, acetic acid, alkali bromide and alkali bromate.

2. Etching solution according to claim 1, wherein the alkali bromide and the alkali bromate are sodium bromide and sodium bromate.

3. Etching solution according to claim 1 or 2, wherein the molar ratio HF/HNO_3 is from 1:1 to 1:15.

4. Etching solution according to claim 1, 2 or 3, wherein bromide and bromate are present in a molar ratio of 5:1.

5. Etching solution according to claim 1, 2, 3 or 4, wherein the molar ratio HF/Acetic is from 1:5 to 1:15.

6. Method for etching silicon surfaces, comprising the step of treating the silicon surface with an etching solution according to any of claims 1 to 5.

7. Method according to claim 6, wherein the silicon surface is a SOI or a sSOI substrate.

8. Method according to claim 6 or 7, wherein the method further comprises a pretreatment of the silicon surface with HF.

9. Method according to claim 6, 7 or 8, wherein the method further comprises a post-treatment of the silicon substrate by rinsing with deionized water and dipping in a HF 49% solution for 90s for defects delineation.

10. Method for characterizing defects on silicon surfaces, comprising the method of claims 6 to 8.

11. Method according to claim 10, wherein the method further comprises a post-treatment of the silicon substrate by rinsing with deionized water.

12. Method in accordance with claim 10 or 11, further comprising the step of visually evaluating the treated silicon surface.

13. Method according to claims 6, 7, 8, 9, 10, 11 or 12, wherein the step of treating the silicon surface with an etching solution according to any of claims 1 to 5 is conducted at a temperature of from 5° C to 25° C.