Process for cleaning a semiconductor wafer using a cleaning solution

The invention relates to a process for cleaning a semiconductor wafer using a cleaning solution, more precisely a process in which the semiconductor wafer is cleaned in an individual-wafer treatment mode.

Individual-wafer cleaning processes have some advantages over multiwafer cleaning processes, in which a plurality of wafers are cleaned simultaneously. These advantages include a low consumption of chemicals, a higher process flexibility and also the possibility of treating the wafer front side and the wafer rear side using different cleaning solutions. A particular advantage of the individual-wafer treatment is that the risk of cross-contamination, that is to say the transfer of contaminants between semiconductor wafers, is precluded. The essential disadvantage of these processes in comparison with the multiwafer treatment is the low throughput. Since silicon wafers having a very large diameter (300 mm) are increasingly being processed in the semiconductor industry, this advantage is receding into the background, however. The individual-wafer cleaning can be effected according to two fundamentally different processes. Thus, the cleaning solution can be provided as a bath into which the semiconductor wafer is dipped for a certain time. More often, an alternative arrangement is used in which the semiconductor wafer is anchored on a rotating plate and the cleaning solution is injected or sprayed onto one or both lateral surfaces of the semiconductor wafer through nozzles. The spent cleaning solution flows away from the semiconductor wafer under the influence of centrifugal force. One example of such an individual-wafer treatment, which is also suitable for etching a semiconductor wafer, is described in US 2004/0031503 A1, for example.

In particular semiconductor wafers on which one or a plurality of further layers are intended to be deposited epitaxially have to have particularly intensively cleaned surfaces prior to deposition. Contaminants that have to be removed are particle contaminants, metal ions bound on the surface, and organic compounds that often cover semiconductor wafers as a thin surface film. Basic solutions of ammonia and hydrogen peroxide in water (ammonium peroxide mixture, APM) are normally used for removing particles and organic compounds. A central prerequisite for the deposition of high-quality epitaxial layers is complete removal of the amorphous oxide layer coating the surface of semiconductor materials such as silicon, germanium and silicon/germanium alloys. The surface oxide is dissolved using aqueous solutions containing hydrogen fluoride, HF. A semiconductor wafer treated using an HF solution has a hydrophobic, oxygen-free surface. A cleaning solution which is particularly suitable for this purpose on account of its high etching rate for silicon dioxide contains a mixture of ammonium fluoride, NH_4F, or a tetraalkylammonium fluoride, e.g. tetramethylammonium fluoride $N(CH_3)_4F$, and hydrogen fluoride. WO 98/56726 A1 shows that it is advantageous for the cleaning solution not to be prepared until directly prior to use, from ammonium hydroxide or tetraalkylammonium hydroxide and hydrogen fluoride.

It is an object of the present invention to present a cleaning process which has an improved cleaning effect over and above the advantages of the individual-wafer treatment and the preparation of the cleaning solution at the site of its use.

The invention relates to a process for cleaning a semiconductor wafer using a cleaning solution containing an ammonium-alkaline component in an initial composition, wherein the semiconductor wafer is brought into contact with the cleaning solution in an individual-wafer treatment, and in the course of cleaning

hydrogen fluoride is added as further component to the cleaning solution, and the cleaning solution has at the end of cleaning a composition that differs from the initial composition.

The process is distinguished by the fact that the composition of the cleaning solution is changed in the course of cleaning, in order to control the cleaning mechanism in a targeted manner. At the start of cleaning, the cleaning solution contains the ammonium-alkaline component but no HF. In the course of cleaning, hydrogen fluoride is added as further component to the cleaning solution. What is thereby achieved is that firstly conditions are created which are optimal for dissolving particles from the semiconductor wafer and permanently transferring them into the cleaning solution, and later conditions are established which are optimal for permanently removing metals from the semiconductor wafer and completely stripping away the oxide film on the surface. The overall result is an improved cleaning effect compared with the use of a fixedly preset composition of the cleaning solution, even if the cleaning solution, as in the process according to the invention, too, is not prepared until at the site of use.

The change in the concentration of the cleaning solution is controlled such that the ratio of the molar concentrations of hydrogen fluoride and ammonium-alkaline component, HF:NR_4OH, is less than 1 at the start of cleaning and is greater than 1 at the end of cleaning. R represents the radicals H or a C_{1-4} alkyl group, where tetramethylammonium hydroxide ($N(CH_3)_4OH$, TMAH) is preferred over ammonium hydroxide (NH_4OH) and the longer-chain tetraalkylammonium hydroxides. The concentration of the ammonium-alkaline component in the cleaning solution is preferably 0.001 to 25% by weight at the start of cleaning, and preferably 0.001 to 10% by weight at the end of cleaning. The concentration of HF in the cleaning solution is preferably 0.01 to 25% by weight at the end of cleaning. The molar quantitative

ratio HF:NR_4OH is preferably between 1.1 and 100 at the end of cleaning. As the proportion of hydrogen fluoride in the cleaning solution increases, the pH of said cleaning solution decreases and changes from a pH in a strongly basic range to an acidic pH in the range from pH 1 to 5. The cleaning of particles is predominant in the basic range and the cleaning of metals is predominant in the acidic range. As a result of the excess of hydrogen fluoride over the ammonium-alkaline component at the end of the cleaning process a solution arises which dissolves the surface oxide on the semiconductor wafer. Ammonium ions adsorb particles stripped away from the semiconductor wafer and thus prevent recontamination of the semiconductor wafer in the further course of cleaning.

In the preferred configuration of the process, the semiconductor wafer is firstly brought into contact with a cleaning solution containing TMAH but no HF. This takes place in a device suitable for an individual-wafer treatment, for example in a bath with overflow or in a centrifuge. It is not until in the further course of cleaning that hydrogen fluoride is added to the cleaning solution, in which case HF is added in one or a plurality of steps or continuously. In the case of cleaning in a bath, an aqueous solution containing TMAH is initially provided and the semiconductor wafer is dipped therein. Later a cleaning solution having a changed composition is prepared in the bath by further TMAH solution and an aqueous HF solution being introduced simultaneously into the bath in the presence of the semiconductor wafer. The concentrations and inflow rates of TMAH and HF are set independently of one another and changed, if appropriate, in the further course of cleaning. Thus, the concentration of HF in the cleaning solution can be increased further for example solely by way of the inflow rates, by increasing the inflow rate of HF solution in comparison with the inflow rate of TMAH solution or conversely by decreasing the inflow rate of TMAH solution in

comparison with the inflow rate of HF. The corresponding case occurs during cleaning of the semiconductor wafer on the plate of a centrifuge. Firstly, an aqueous solution which contains TMAH and is supplied via one or a plurality of nozzles is squirted or sprayed onto one or both lateral surfaces of the semiconductor wafer rotating on the plate. Later, a cleaning solution having a changed composition is prepared on the semiconductor wafer by aqueous HF solution additionally being supplied to the semiconductor wafer through one or a plurality of further nozzles. In this preferred embodiment of the invention, too, the concentrations and inflow rates of TMAH solution and HF solution are set independently of one another and changed, if appropriate, in the further course of cleaning.

The preferred duration of the cleaning phase with a cleaning solution which as yet contains no HF is 1 to 300 s, particularly preferably 5 to 30 s. The concentration of TMAH in the cleaning solution is preferably 0.001 to 25% by weight in water. In order to further improve the performance with respect to removing particles, the cleaning solution can contain surfactants or short-chain alcohols in this phase, in particular. Suitable surfactants are, in particular, anionic or nonionic detergents, e.g. fatty alcohol ethoxylates or long-chain alkylsulfonates. Suitable alcohols are e.g. butanol, ethylene glycol or glycerol. The cleaning solution should not contain ozone, hydrogen peroxide or any other oxidizing agent.

The concentration of aqueous HF supplied later is preferably 0.01 to 50% by weight in water. The preferred duration of the phase of cleaning the semiconductor wafer using a cleaning solution which contains HF is 1 to 300 s, particularly preferably 5 to 30 s.

The temperature of the cleaning solution is 15 to 95°C, preferably 15 to 45°C, in both phases.

At the end of the process according to the invention, the surface of the semiconductor wafer is hydrophobic and free of surface oxide. For further treatment, the semiconductor wafer can be rinsed with another cleaning solution, for example with deionized water, and subsequently dried. However, it is also possible to return to the starting point of the process and to repeat the process once or more often, by the semiconductor wafer being cleaned again using the cleaning solution in the initial composition.

Semiconductor wafers for which the cleaning process presented is particularly suitable are, in particular, semiconductor wafers having a surface composed of silicon or an alloy of silicon and germanium which is to be cleaned in order to be coated later.

Patent Claims

1. A process for cleaning a semiconductor wafer using a cleaning solution containing an ammonium-alkaline component in an initial composition, wherein the semiconductor wafer is brought into contact with the cleaning solution in an individual-wafer treatment, and in the course of cleaning hydrogen fluoride is added as further component to the cleaning solution, and the cleaning solution has at the end of cleaning a composition that differs from the initial composition.

2. The process as claimed in claim 1, wherein a molar concentration ratio of hydrogen fluoride to ammonium-alkaline component, $HF:NR_4OH$, of < 1 at the start of cleaning is changed up to > 1 at the end of cleaning, wherein R represents the radicals H or methyl, ethyl, propyl or butyl.

3. The process as claimed in claim 1 or claim 2, wherein hydrogen fluoride is added to the cleaning solution and the concentration of the ammonium-alkaline component is reduced.

4. The process as claimed in any of claims 1 to 3, wherein the cleaning solution contains surfactants or short-chain alcohols as further components.

5. The process as claimed in any of claims 1 to 4, wherein the cleaning solution contains no ozone or hydrogen peroxide.

6. The process as claimed in any of claims 1 to 5, wherein the cleaning solution is injected or sprayed onto the rotating semiconductor wafer through nozzles.

7. The process as claimed in any of claims 1 to 5, wherein the cleaning solution is conducted into a bath into which the semiconductor wafer is dipped.

8. The process as claimed in any of claims 1 to 7, wherein the cleaning is repeated at least once by the semiconductor wafer being cleaned again using the cleaning solution in the initial composition.