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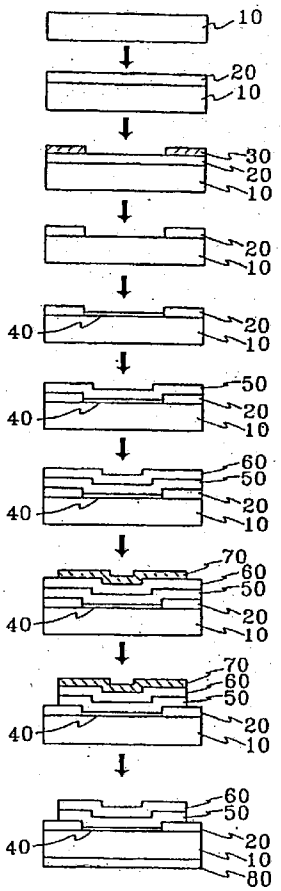
(54) Title: SOLUTIONS FOR CLEANING SILICON SEMICONDUCTORS OR SILICON OXIDES



(57) Abstract: A solution for cleaning silicon semiconductors or silicon oxides, and methods for cleaning silicon semiconductors or silicon oxides using the solution, is disclosed. The solution includes hydrogen peroxide, ammonium hydroxide, an alkanolamine, and at least one of a tetraalkylammonium hydroxide, an alkanolamide, an amido-betaine, an c ca dihydroxyphenol, a carboxylic acid, a phosphonic acid, a chelating agent or a surfactant. The weight ratio of ammonium hydroxide to peroxide to water is between about 1:1:5 and 1:1-4:50, the weight ratio of ammonium hydroxide to water is between 1:5 and 1:50, and the molar ratio of component A to ammonium hydroxide is between 1:10 and 1:5000 is disclosed. The solution can achieve the efficiency equivalent to that of the conventional RCA two-step cleaning solution within a shorter time by one step preserving the silicon and silicon oxide substrate integrity and effectively remove contaminants such as organics, particles and metals from the surfaces of silicon semiconductors and silicon oxides without using strong acids such as HCI and sulfuric acid.

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SOLUTIONS FOR CLEANING SILICON SEMICONDUCTORS OR SILICON OXIDES

Field of the Invention

[0001] The present invention pertains to solutions for cleaning silicon semiconductors or silicon oxides. More specifically, the present invention provides solutions which can remove contaminants such as organics, particles and metals from the surfaces of silicon semiconductors and silicon oxides by one step.

Background of the Invention

[0002] The fabrication of devices beyond current scaling imposes alternative cleaning solutions to the traditional RCA cleaning to comply with the specs for particles, metals, organic and material (silicon and silicon oxide) loss, as published by ITRS surface preparation road map as requirements at 65nm-technology node and beyond.

[0003] There are continuous efforts in the art of production of silicon semiconductors and micro-circuits to meet the requirements associated with the new leading edge devices. The cleaning steps are responsible for surface preparation and for controlling surface contamination, which is critical for device performance, reliability and cost. The increased fragility of the scaled and new device structures is limiting the aggressiveness of the cleaning processes that may be employed.

[0004] In 1970, RCA (Radio Corporation of America) developed an effective cleaning system for removing contaminants from surfaces of silicon semiconductors and silicon oxides. The system comprises two cleaning steps. An aqueous solution comprising hydrogen peroxide and ammonium hydroxide is used in the first step to remove organic contaminants. Since the solution may inevitably cause contamination with heavy metals such as Fe, Zn and Al which are trace metal contaminants in the solution, a solution containing HCl must be used in the second step to remove the metal contaminants. According to the RCA system, an effective cleaning operation comprises using a solution comprising 5:1:1 to 7:2:1 by volume of water/30% hydrogen peroxide /27% ammonium hydroxide in the first step for 10 to 20 minutes and using a solution

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comprising 6:1:1 to 8:2:1 by volume of water/30% hydrogen peroxide /37% HCl in the second step for 10 to 20 minutes. The Standard Clean-1, SC-1 (RCA-1) function is to remove the organic and particle contaminants, while the Standard Clean-2, SC-2 (RCA-2) function is to remove the metallic contaminants. In other words, RCA system must use strong acid chemicals such HCl, involves two steps and needs at least 20 minutes for cleaning.

[0005] Though RCA system can effectively remove heavy metal contaminants from the surfaces of wafers, particles contained in the acidic cleaning solution which comprises HCl will stick to and contaminate the surfaces. Further, RCA system involves two separate steps and this is an inconvenient operation. Persons in semiconductor device and silicon wafer in particle sries continuously search for new formulations to replace RCA system to provide an easier, more effective and more economical cleaning system.

[0006] Various approaches have been developed to replace the RCA system and most of them are directed to the cleaning solution of the second step. Japanese Patent KOKAI (Laid-Open) No. Sho 58-30135 discloses the use of an acidic aqueous solution containing HF, sulfuric acid and hydrogen peroxide. Japanese Patent KOKAI (Laid-Open) No. Hei 2-100320 discloses the use of a combination of a mixture of ammonium hydroxide and hydrogen peroxide in water and a mixture of HCl and hydrogen peroxide in water. A solution of strong acid and a very small amount of a compound containing fluorine is disclosed in Japanese Patent KOKAI (Laid-Open) No. Hei 4-234118. A solution containing 0.50% HF and 0.1 to 1% hydrogen peroxide is disclosed in "TRYBOROZIST" Vol. 37, No. 3, (1992) pp. 218-224 and the cleaning is conducted at room temperature. U.S. Pat. No. 5,560,857 discloses the use of an aqueous acidic solution containing 0.005% to 0.05% by weight HF and 0.3% to 20.0% by weight hydrogen peroxide and having a pH in the range from 1 to 5. In other words, most modifications on RCA system are directed to the substitution of the solution used in the second cleaning step.

[0007] However, as mentioned above, in addition to the shortcoming of particle contamination, RCA system further has the disadvantages of an inconvenient operation (involving two steps and requiring at least 20 minutes) and the use of strong acid chemicals. All the aforementioned known approaches cannot avoid these disadvantages. There is a necessity in the art of an effective cleaning system to simplify the RCA

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system, avoid the use of strong acid chemicals and meet the simple, effective and economical requirements.

Summary of the Invention

[0008] Cleaning solutions that can significantly reduce the cleaning time, simplify the cleaning procedures and avoid using strong acid chemicals are disclosed, as well as methods for using the compositions to clean silicon semiconductors or silicon oxides are disclosed. The silicon semiconductors are present, for example, in semiconductor integrated circuit devices. Integrated circuit elements with good key device electrical performance and charge to breakdown and breakdown field properties that are superior to those cleaned by RCA systems are also disclosed.

[0009] The solutions include hydrogen peroxide, ammonium hydroxide, an alkanolamine, and at least one of a component A selected from a tetraalkylammonium hydroxide, an alkanolamide or amido-betaine, an α,α-dihydroxyphenol, a carboxylic acid or a phosphonic acid or their salts, a chelating agent and a surfactant.

[0010] The weight ratio of ammonium hydroxide to peroxide to water is typically between about 1:1:5 and about 1:1:100, and the molar ratio of component A to ammonium hydroxide is between 1:10 and 1:1000. The alkanolamine is typically present in a ratio of about 0.1 to about 10 percent by weight, more typically in a range of about 0.1 to about 5 weight percent.

[0011] In one embodiment, the solution includes substantially no fluoride ions, and in this embodiment, the amount of surface etching of the substrate to be cleaned is minimized. In this embodiment, the amount of etching/material loss by etching is less than about two angstroms, whereas a comparable solution with the same components, to which fluoride is added, typically results in a material loss of more than twenty angstroms.

[0012] The methods of cleaning involve contacting the substrate to be cleaned with the solutions described herein for a sufficient amount of time to remove contaminants, such as organics, particles and metals from the surfaces of the substrates. In one embodiment, the methods further involve mechanical cleaning steps, although these often result in additional material loss.

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