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Metal Removal from a Silicon Surface by UV Irradiation in Pure Water

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A new wet cleaning method using pure water and ultraviolet light has been investigated. This method, the PW/UV cleaning, is simply irradiating a pure water coated silicon wafer with ultraviolet light. The metal removal efficiency was evaluated for transition metals adsorbed on hydrophilic surface and copper deposited on hydrophobic surface. It was found that the PW/UV cleaning has high efficiency for metal removal without any reactive chemicals and gases.

1. Introduction

Wafer cleaning processes have been widely used in LSI fabrication. Typical wet cleaning, such as RCA cleaning[1], utilizes mixed solution of hydrogen peroxide, hydrogen chloride, and ammonium hydroxide. Greater amount of these chemicals are expected to be necessary as the larger diameter wafers are used and process steps increase for the fabrication of higher density ULSI. The higher purity of the chemicals will also be required, which can result in the enormous increase in the cleaning cost.

Therefore, it is an urgent need to develop a new cleaning process with less or no chemicals. A number of cleaning methods using the photochemical reaction have been tried to remove contaminants, but most of these cleaning methods are restricted to a organic contamination removal with ozone ambient generated by photoreaction[2].

Douglas and Gnade have reported that evaporated metal on a silicon wafer could be removed by irradiation with ultraviolet light in water[3]. It was not clear, however, that ultraviolet irradiation could be effective for removing chemically contaminated metals on a silicon wafer.

We have studied the effect of ultraviolet irradiation on the metal removal on more actual silicon surface. We have found that ultraviolet irradiation in pure water had good removal efficiency of chemically contaminated metals on silicon wafer.

2. Experimental

2-1. Apparatus

The cleaning apparatus used in the present work is schematically shown in Fig. 1. The apparatus consists of a wafer rotating stage, water/gas supplying nozzles within a chamber, and a low pressure mercury lamp as the source of a ultraviolet light of 80 mW/cm^2 (wavelength of 254 nm) at the top of the chamber. The air in the chamber can be purged by the oxygen, nitrogen or argon, after exhaust by a ejector pump. The ambient contained residual oxygen less than 2% after the replacement to nitrogen or argon gases, and the pure water at a use point contained only 50 ppb oxygen, which was low enough to keep a bare silicon surface.

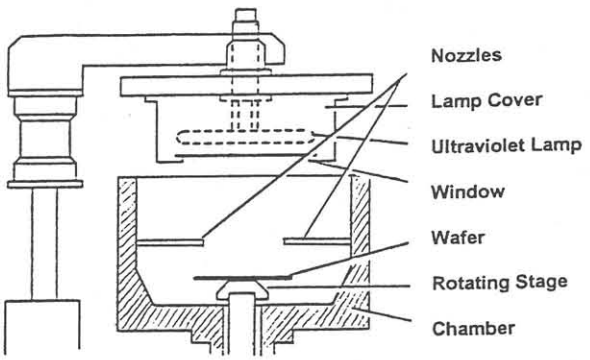

Fig. 1 The schematic diagram of the apparatus.

2-2. Cleaning sequence

The wafer cleaning sequence is shown in Fig. 2. A wafer was loaded into the chamber, supplied pure water onto the surface, and irradiated with ultraviolet light through the pure water. On the wafer surface, the pure water was remaining with 2-4 mm thickness because of the surface tension during the cleaning. The wafer was

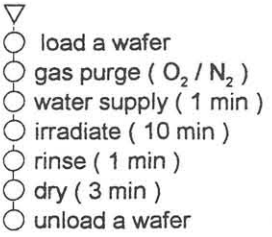

Fig. 2 The experimental sequence

dried by spinning with a blowing after pure water rinsing in the chamber. No chemicals were used in this cleaning. The metal concentration on the intentionally contaminated silicon surface before and after the cleaning sequence was measured by Total REflection X-ray fluorescent spectroscope (TREX) for the transition metals

2-3. Contamination of silicon wafer with metals

Both n-type and p-type Si (100) wafers were used for evaluation of the contamination removal efficiency.

The metal contaminated silicon wafer were prepared by being immersed in nitrate solution containing metal ions such as chromium, iron, nickel, copper, and zinc. After this intentionally contamination, silicon surface becomes hydrophilic. For copper, contamination from hydrofluoric acid solution containing copper ion was also made. In this case, the surface become hydrophobic after contamination.

3. Results and Discussion

3-1. Removal of adsorbed metal on hydrophilic silicon surface by PW/UV cleaning.

Figure 3 and 4 show the metal concentration after the PW/UV cleaning as a function of the initial metal concentration with ultraviolet light off and on, respectively. These results indicate that the metal contaminants which were chemically adsorbed on a wafer, were scarcely removed in pure water only, whereas the ultraviolet irradiation had enhanced removal of the metals. This implies ultraviolet irradiation in pure water stimulates the desorption of the metals on the silicon surface. The enhancement was stronger in the oxygen ambient than in the nitrogen ambient.

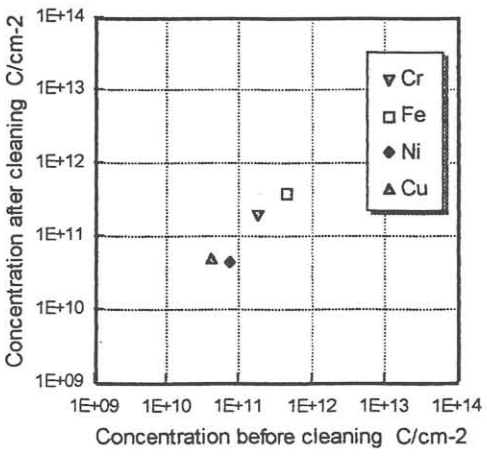

Fig. 3 Removal of adsorbed transition metals in pure water in oxygen ambient without UV light.

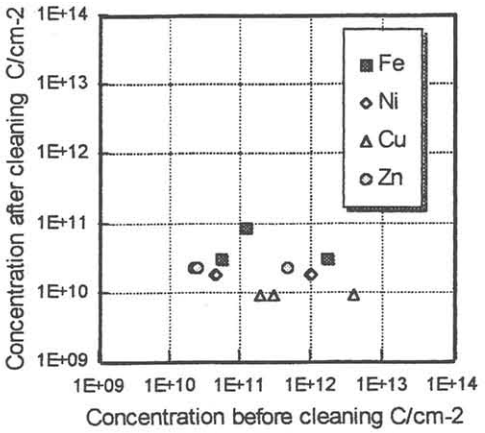

Fig. 4 Removal of adsorbed transition metals by UV irradiation in pure water in oxygen ambient.

3-2. Removal of deposited copper on hydrophobic silicon surface by PW/UV cleaning.

A hydrophobic surface of wafer was contaminated by copper from hydrofluoric acid solution, which makes the copper deposit onto the silicon surface as a form of metal[4], not as a oxide. A preoxidation process was investigated whether the oxidation has an additional effect to the copper removal or not. The copper-contaminated wafer was oxidized for 0-15 min by ultraviolet irradiation in oxygen before the PW/UV cleaning. Figure 5 shows the residual concentration of copper after the PW/UV cleaning as a function of preoxidation time. It indicates the preoxidation has an additional enhancement of the removal of copper deposited on the hydrophobic silicon surface.

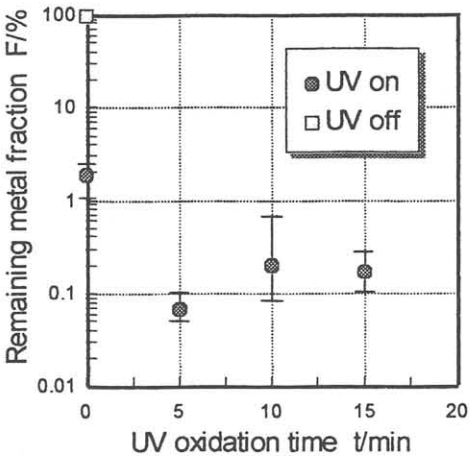

Fig. 5 Removal of deposited copper by UV irradiation in pure water.

Thus, it is considered that the oxidation is probably an important factor to remove a deposited copper contamination from a silicon surface. In fact, the VPD/AAS[5] for trace metal analysis of a thermal or native oxide layer, has a good recovery ratio of contaminants even for the copper, more than 90%.

3-3. Recontamination and effect of continuous supply of water.

Figure 6 shows the dependence of metal concentration on the hold time of pure water after the PW/UV cleaning for intentionally contaminated wafers. Iron concentration on the surface increased after holding the pure water for 5 or 10 minutes, whereas nickel, copper, and zinc did not exhibit almost no increase in the surface concentration. This means that some fraction of iron atoms, which was desorbed from the surface by ultraviolet irradiation and diffused into the pure water, recontaminated the surface after ultraviolet light off.

Therefore the cascade PW/UV cleaning was tried to prevent a recontamination from the solution on a wafer. The pure water is cascaded onto a wafer with 0.2 L/min from nozzle. At the same time, the wafer is rotated 10 min^{-1} under the ultraviolet irradiation for a homogeneous cleaning. This condition was applied to the metal removal from a contaminated wafer by nitrate solution.

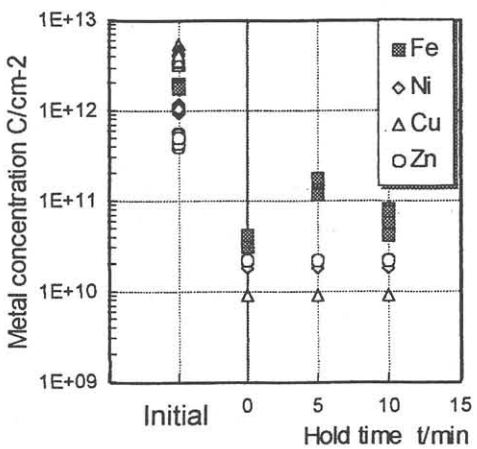

Fig. 6 Correlation between hold time after irradiation and recontamination.

The iron was removed below the detection limit (3 x 10^{10} cm^{-2}) even in a high initial contamination level of 3 x 10^{12} cm^{-2}, when the cascade rinsing was applied to the PW/UV cleaning. It shows that the cascade rinsing with the ultraviolet irradiation is effective to prevent recontamination from the solution, especially for iron.

4. Conclusion

a) It was confirmed that transition metal contaminants on silicon wafer can be effectively removed by UV irradiation in pure water without any chemicals.
b) The preoxidation of silicon surface by ultraviolet irradiation in oxygen ambient before the PW/UV cleaning have an additional effect to remove the copper which is deposited form hydrofluoric acid onto a hydrophobic surface.
c) The PW/UV cleaning with continuous supply of water can prevent the recontamination of metal during the cleaning.

5. Reference

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