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# The Cleaning of Particle and Metallic Impurity on Si Wafer Surface by Fluorine Etchant

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We have studied the new cleaning method of Si Wafer surface. The cleaning solution is surfactant added $HF/H_2O_2/H_2O$ solution exited by the megasonic vibration. This method can remove particles and metals simultaneously without the increasing of the surface microroughness at the room temperature. On the other hand, we evaluated the $O_3$ water cleaning, and it was found that most of metallic impurities was able to removed by the $O_3$ water cleaning. The combination of these two cleaning methods becomes to possible to decreasing of the number of process step.

## 1. Introduction

The importance of ULTRACLEAN concept has been demonstrated by various experimental data [1]. To realize ULTRACLEAN WAFER SURFACE, the RCA cleaning method which was established by W.Kern et al. has used for long time [2]. However, the RCA cleaning method uses many kinds of chemicals and is conducted at high temperature. Moreover, it is reported that $HCl/H_2O_2$ cleaning in RCA cleaning enhances Cu adhesion [3]. We believe that the wet cleaning should be conducted at the room temperature and decreasing kinds of chemicals. On the other hand, many new cleaning methods was proposed [4,5]. Especially, diluted $HF/H_2O_2$ cleaning in place of DHF cleaning is effective to remove noble metals such as Cu. During our study of this cleaning, we have found that diluted $HF/H_2O_2$ solution causes increasing the surface microroughness of the silicon surface.

In this report, we propose new cleaning method using surfactant added $HF/H_2O_2$ solution exited by megasonic vibration.

## 2. Experimental

5 inch phosphorus doped n-type CZ Si(100) and 4 inch n-type CZ Si(100) wafer were used for evaluations of metallic impurity and particles. The component and composition of chemicals used in this experiment are shown as follows:

DHF: 0.5wt% aq. (25°C)
SPM: $H_2SO_4$(98wt%)/$H_2O_2$(30wt%)=4:1 (120°C)
FPM: 0.5wt%HF/10wt%$H_2O_2$/$H_2O$ (25°C)
FPMS: FPM+Surfactant(50ppm) (25°C)

And 0.95MHz MegaSonic(MS) was used as the vibration source in our experiment. All cleaning was carried out for 10 min. Atomic force microscope (AFM) was employed to evaluate the microroughness of Si surface. The metallic contamination level on Si surface was measured with Total Reflection X-Ray Fluorescence Spectroscopy (TRXRF) with an incident angle of 0.05°. Particle counts on wafers were evaluated using an Aeronca WIS-100 wafer inspection system. The WIS-100 classifies defects as particles(>0.5μm) or haze(particles <0.5μm). All wafers for experiments were first cleaned by SPM and DHF cleaning. For metal removal experiments, these wafers were contaminated in the water for 3 min which was added 1ppm Cu ions. $CuCl_2$ is used in this experiment. For particle removal experiments, the following particles were used: (a) Polystyrene latex(PSL) spheres having a diameter of 0.22μm; (b) Particles from 50% tap(city) water and 50% ultra pure water mixed which was added 100ppb Cu ions.

## 3. Results and Discussion

Figure 1 shows the relationship between the immersing time into FPM or FPMS solution of the wafer and the surface microroughness. It is clearly seen that the surfactant in the FPM solution is effective to inhibit the increasing the surface microroughness. When the surface was contaminated with noble metals such as Cu, it kept the smoothness after FPMS cleaning. It seems that FPMS solution has good wettability, the silicon is oxidated and etched with $H_2O_2$ and HF uniformly. The effect of the addition of the surfactant on the cleaning was studied as shown in Fig.2. The difference of cleaning efficiency of FPM and FPMS solutions was not observed, and the cleaning time for 10 min was sufficient. For cleaning of metallic particles, these particles should be dissolved into solution as cations and prevented re-adhesion of cations from solution onto Si wafer surface. In order to realize these phenomena, the solution that has high redox potential is required. When the cleaning solution has higher redox potential than metals, metals release electron to solution and solve into solution as cations. We can speculate that FPM solution has higher redox potential than metals. It was reported that $O_3$ water cleaning was the effective cleaning method for organic removal [6]. This $O_3$ water cleaning is effective for metal removal not only organic, because this solution has high redox potential.

Next, we have evaluated the particle removal efficiency of some solutions. Figure 3 shows the number of particles(PSL) before(Initial) and after the cleaning. DHF and FPM solutions can not remove particles. FPMS solution removes particles more than 0.5μm. FPM and FPMS with MS is more effective to remove particles than other cleaning without MS. The addition of the surfactant inhibits the deposition of particles not only the surface microroughness. Figure 4 shows the map of particles on Si wafer after FPM and FPMS with MS cleaning. It is clearly seen that most of particles deposit around the bottom after FPM with MS cleaning. We can think that these particles deposit again during pulling up the wafer from the solution. The addition of the surfactant is very important to inhibit re-adhesion of particles.

The particles and metals from tap water removal efficiency was evaluated, as shown in Fig.5. In this experiment, we evaluated $O_3$ water, FPMS and FPMS with MS cleaning methods. Figure 5 shows the number of particles before and after the cleaning. The FPMS with MS cleaning after $O_3$ water cleaning is more effective than only FPMS with MS cleaning. It is well known that the organic impurity is removed by $O_3$ water. In addition, most of metallic contamination can removed by $O_3$ water. $O_3$ water cleaning is effective to remove metals too. So we recommend the combination of $0_3$ water and FPMS with MS. The surface microroughness, which was contaminated with the tap water and cleaned by $O_3$ water and FPMS with MS, was measured, as shown in Fig.6. It was confirmed that the surface microroughness was not changed before and after the cleaning.

We propose a new cleaning procedure as shown in Table 1. This cleaning method is consist of $O_3$ water and surfactant added $HF/H_2O_2$ solution at room temperature.

## 4. Conclusion

We have evaluated the new cleaning method of the silicon surface. The solution is $HF/H_2O_2/H_2O$ with the surfactant. We use this solution with Megasonic vibration, it becomes to possible to remove particles and metallic impurities simultaneously without the increasing of the surface microroughness. This cleaning method realize the low temperature process, decreasing of the number of process step and decreasing of chemicals.

## 5. Reference


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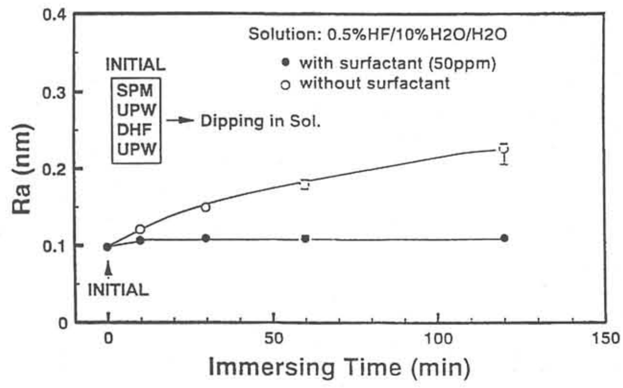


Fig.1. The relationship between the immersing time and the surface microroughness.

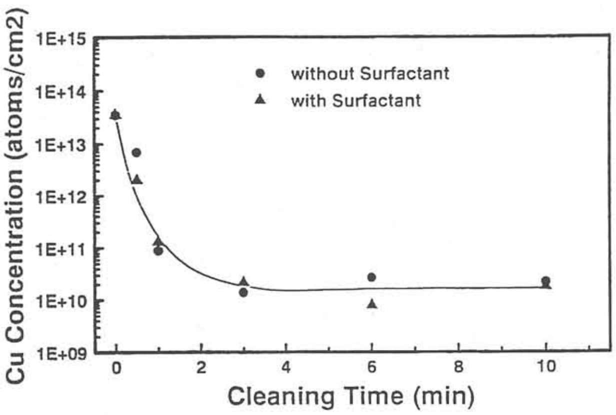


Fig.2. The relationship between the cleaning time and Cu concentration on the silicon surface. The cleaning solution is $HF/H_2O_2/H_2O$ with and without surfactant.

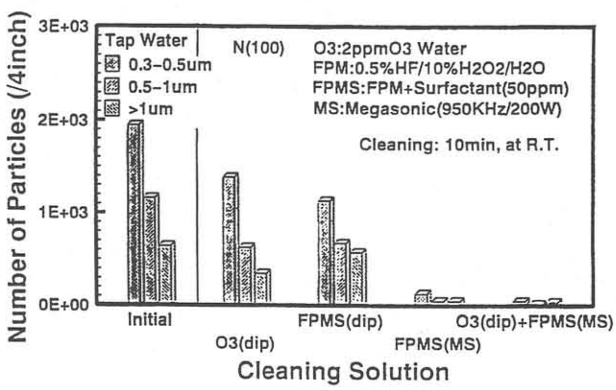


Fig.5. The number of particles from the tap water before and after the cleaning.

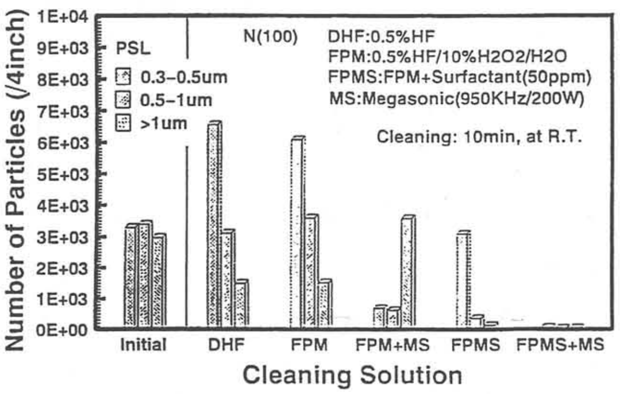


Fig.3. The number of particles on the silicon surface before and after the cleaning. Particles are Polystyrene latex spheres.

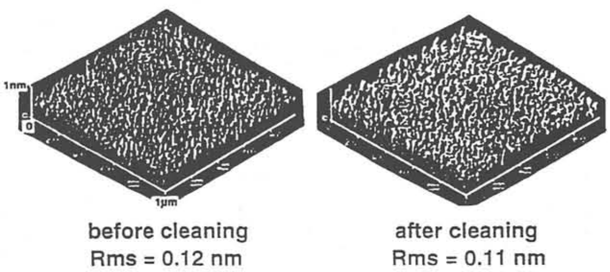


Fig.6. AFM images of the silicon surfaces before and after cleaning. The cleaning is FPMS with MS after $O_3$ water cleaning.

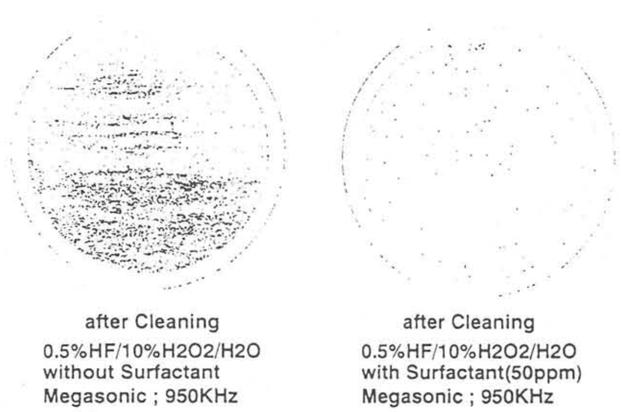


Fig.4. The map of particles after the cleaning.

Table. 1. Novel Wet Chemical Sequence at Room Temperature Totally.

| Step # | Process | Cleaning Targets |
|---|---|---|
| 1 | $O_3/H_2O$ | Organic, Metal |
| 2 | $HF/H_2O_2/H_2O$ +Surfactant +Megasonic | Particle Chemical Oxide Metal |
| 3 | Shower Rinse (UPW) | Chemical |
| 4 | $O_3/H_2O$ | Surfactant |
| 5 | DHF | Chemical Oxide |
| 6 | UPW Rinse | |