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Ultra Clean Surface Preparation Using Ozonized Ultrapure Water

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The wet process is still employed to clean the wafer surface due to its superior characteristics : it does not cause any damages on the wafer and it can function at low temperature. The technology of ozone-injected ultrapure water is capable of effectively removing organic contaminants on the wafer surface in short time and at room temperature. We propose the replacement of the widely used ($H_2SO_4/H_2O_2/H_2O$)(SPM) cleaning process by a newly developed ozonized ultrapure water cleaning.

1. Introduction

The preparation of an ultraclean wafer surface is essentially important to establish advanced process technologies for ULSI manufacturing. In order to develop devices with higher performance, therefore, it is essential to realize a contamination-free wafer surface[1)]. The ultraclean wafer surface can be realized by perfectly controlling the following six elements :

1) Particle free
2) Metallic contaminant free
3) Organic contaminant free
4) Native oxide free
5) Surface smoothness
6) Hydrogen-terminated surface

The current wet process is based on the RCA cleaning method which W.Kern et al developed in 1970[2)]. In other words, the wet process has employed the RCA cleaning as its base for more than 20 years. Compared with the semiconductor devices of 20 years ago, however, the current devices feature much higher aspect ratio and complexity, and accordingly an unfavorable effect of surface microroughness of the wafer has been pointed out in recent studies. As a result, the wafer cleaning process presently requires drastic improvements[3-6)]. In this paper, It has been revealed that the ozone-injected ultrapure water process can replace the SPM cleaning in the RCA cleaning as a process to remove organic impurities and that this process will contribute to realization of the closed system as waste drained from this process can be recovered.

2. Growth of native oxide on the Si wafer surface

Figure 1 shows thickness of the native oxide formed on the Si wafer in the ozonized ultrapure water as a function of immersion time. A CZ n-type(100) wafer was employed in this experiment. In a pre-treatment, the wafer was treated with the RCA cleaning. At the end of the RCA cleaning, the wafer went through the 0.5% DHF cleaning for one minute to remove native oxide on its surface. Then the wafer was rinsed with ultrapure water for 10 minutes.

Following the above-mentioned pre-treatment, the sample wafer was immersed into the ozonized ultrapure water for a predetermined time. In this test, we set flow rate of the ozonized ultrapure water at 0.8 l/min and ozone concentration of the ozonized ultrapure water was varied to 2 ppm, 1 ppm, 0.5 ppm 0.1 ppm and 0.04 ppm.

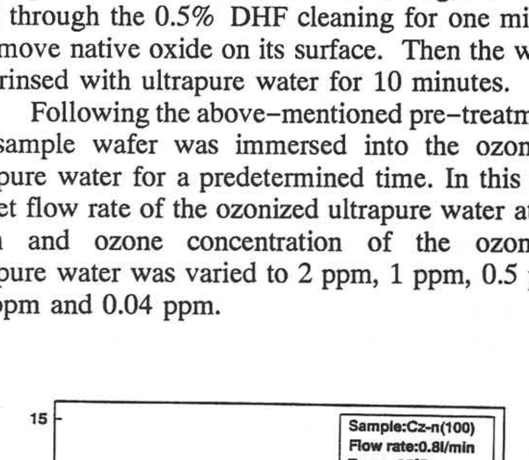


Fig. 1 Native oxide growth on Si surface by dipping ozonized ultrapure water as a function of dipping time and ozone concentration.

As shown in Figure 1, native oxide was found to get grow rapidly at high ozone concentration. In the case of 2 ppm, native oxide was found to saturate in about 10 minutes, where the oxide film thickness was about 10 Å. It has been revealed that, due to oxidation characteristic of high concentration ozone (higher than 0.5 ppm), the Si surface is covered with native oxide in a moment. Surface smooth has been confirmed to be maintained during this ozonized ultrapure water treatment by using AFM (Atomic Force Microscope) in Figure 2.

Figure 3 shows a test to repeatedly form and remove a native oxide on a wafer to see the change in surface roughness. The Ra value scarcely changes even after 20 times of operation. It is confirmed that the native oxide formed in the ozonized ultrapure water grows thick in a short time and that it does not deteriorate the wafer surface.

3. Effect of Residual Organic Impurity on Cleaning Efficiency

Organic impurities adsorbed on the substrate surface must be removed. When organic materials remain on the wafer, it is not able to remove the impurities, such as native oxide and metallic contamination completely. In order to make wafer surface ultra clean, therefore, it is essential to remove organic materials on the surface first of all.

We evaluated the effect of residual organic impurities on the cleaning process by using a surfactant-added developer as an example of residual organic impurities.

Figure 4 shows XPS profile of Si_{2p} for the two wafer samples. A solid line in this figure stands for the sample without the ozonized ultrapure water cleaning while a broken like stands for the one with this cleaning. In the case of the sample without the ozonized ultrapure water cleaning, a peak of SiO_2 is detected on the wafer surface. This peak corresponds to the native oxide formed on the wafer surface. This means the native oxide was not removed in the DHF cleaning. The surfactant once adsorbed on the wafer surface can not be completely removed in the ultrapure water rinsing. When the surfactant remains on the

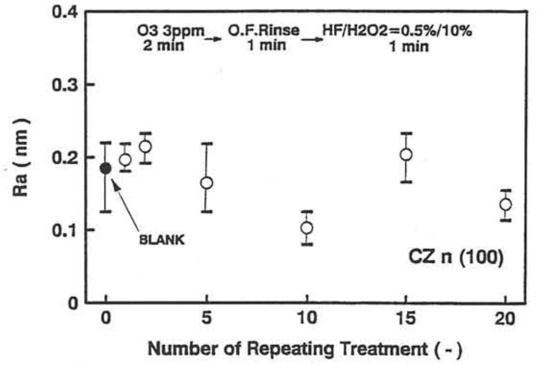


Fig.3 Influence of native oxide formed by ozonized ultrapure water to surface microrougness.

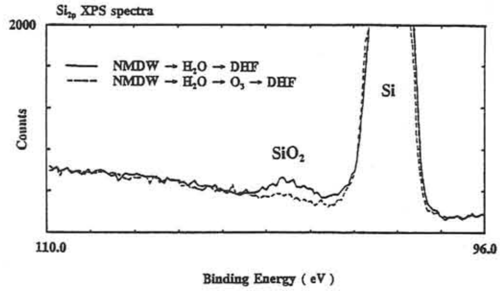


Fig.4 Influence of residual surfactant molecule on Si wafer surface.

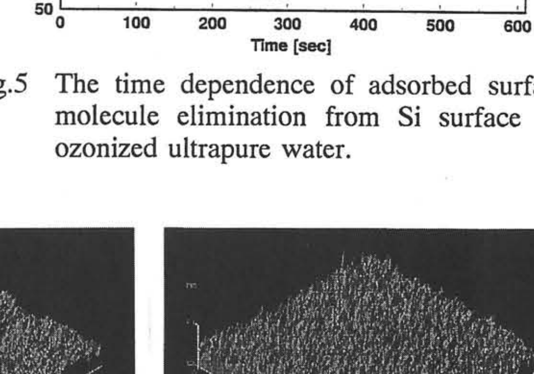
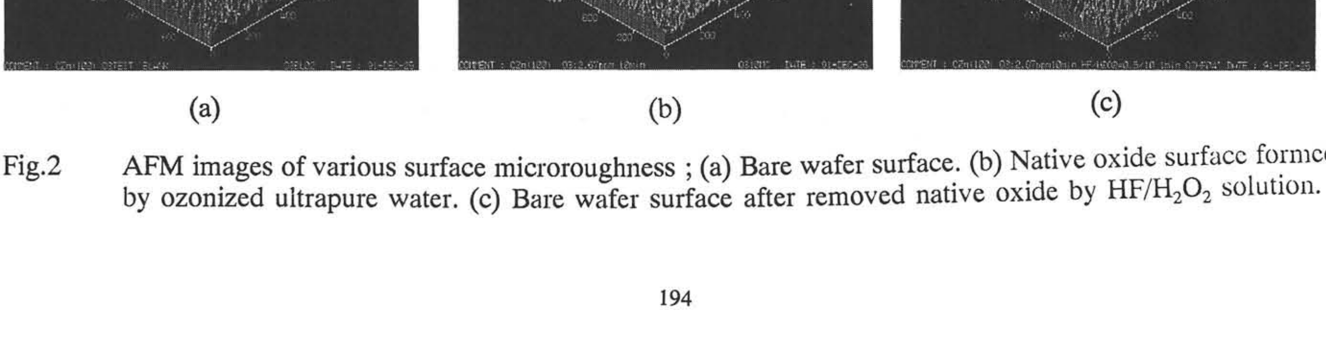


Fig.5 The time dependence of adsorbed surfactant molecule elimination from Si surface using ozonized ultrapure water.



(a) (b) (c)

Fig.2 AFM images of various surface microroughness ; (a) Bare wafer surface. (b) Native oxide surface formed by ozonized ultrapure water. (c) Bare wafer surface after removed native oxide by HF/H_2O_2 solution.

surface, the native oxide is formed between the wafer substrate and the surfactant molecules. Therefore the native oxide can not be completely removed in the DHF cleaning. In other words, as the wafer surface is covered with residual surfactant molecules, the DHF cleaning can not properly function. On the other hand, no native oxide is detected on the wafer sample treated with the ozonized ultrapure water as shown with the broken line. Due to oxidation characteristic of ozone, the surfactant is completely decomposed and removed.

It has been revealed residual organic impurities on the wafer can not be completely removed solely in the ultrapure water rinsing, which leads to an insufficient cleaning of the wafer surface.

4. Organic Impurity Removal with Ozonized Ultrapure Water

In order to evaluate the organic removal capability of ozonized ultrapure water by contact angle, ozone concentrations were changed various values such as 1.5, 0.8, 0.46, 0.28ppm shown in Figure 5. As the ozone concentration in ultrapure water is increased, the contact angle comes back to the initial level in a shorter time. In case of 1.5ppm ozone concentration , organic materials were removed within one minute under the room temperature.

Figure 6 shows XPS profile of C_{1s}. A solid line in this figure indicates XPS profile when the surfactant is adsorbed on the wafer. Two sharp peaks are detected. One at a low binding energy corresponds to C_{1s} while the other at a high binding energy corresponds to what is peculiar to the surfactant. A broken line stands for XPS profile when the wafer is cleaned with the ozonized ultrapure water (ozone concentration of about 2ppm) for one minute. The peak of the surfactant is not at all detected. This means the surfactant adsorbed on the wafer surface is decomposed and removed due to strong oxidation characteristic of ozone.

We have found in our experiment, however, that the surfactant adsorbed on the wafer can be easily

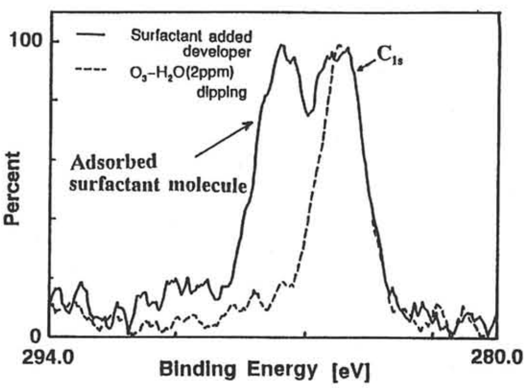


Fig.6 The effect of ozonized ultrapure water cleaning to remove surfactant molecule on Si wafer surface.

removed merely by the 60-second immersion in the ozonized ultrapure water. This method is considered very effective and economical as it does not need high temperature or chemicals.

5. Summary

The conventional RCA cleaning employs the $H_2SO_4/H_2O_2/H_2O$ cleaning to remove organic impurities. This cleaning method, however, has some disadvantages : to require high temperature and processing of chemical wastes. We have tried the ozonized ultrapure water cleaning as a method to remove residual organic impurities. Ozone, when decomposed, generates an oxygen radical which decomposes organic impurities adsorbed on the wafer and forms a native oxide on it. The surfactant added to the developer in the lithography process to improve wettability, tends to remain on the wafer surface even after the development process. This residual surfactant is persistent and can not be removed even in the high-temperature baking. We have found, however, the ozonized ultrapure water is effective in removing this surfactant.

Ozonized ultrapure water cleaning works very effectively to eliminate organic materials from silicon wafer surfaces using the developer including surfactant molecule. It has been demonstrated that ozonized ultrapure water can be replacement of SPM cleaning for ultraclean wafer surface preparation and simplification of wet chemical processing.

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