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Low Dissolved Oxygen Ultrapure Water Systems for Native Oxide Free Wafer Processing

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In the manufacture of submicron or deep submicron ULSIs, it is important to completely suppress the native oxide growth on the silicon wafer surfaces. This has led to the creation of the two ultrapure water supply systems in which uses two-stage to remove dissolved oxygen. Both systems are able to provide ultrapure water with dissolved oxygen suppressed to a level less than 10 ppb. And then impurities like TOC, Silica and Total-residue are also improved to the level less than 1 ppb.

1. INTRODUCTION

The integration of an electronic device has been significantly improved from IC to LSI, and VLSI. As a higher-integration requires a device with smaller demention, the effect of minute contamination on the silicon wafer surface is becoming more and more critical. In order to introduce a complete dry cleaning process, various technologies are being tried such as a vapor etching technology[1] in which native oxide is selectively removed by hydrogen fluoride. Since the present dry process is not perfect enough, however, the metal contamination of 10^{11}-10^{13} atm/cm^2 is observed on the wafer surface[2] and wet process needs to be added after this dry process.

Wet process are therefore very important, and it is now necessary to remove as much impurity as possible from the ultrapure water that comes in direct contact with the wafer in final rinsing.

Meanwhile native oxide grows when a wafer is being rinsed with ultrapure water, when being dried, and when transported to the next process equipment. Native oxide affects high-performance processes in various ways; it affects the low temperature growth of high-quality epitaxial Si and the quality of thin gate oxide, and it raises the contact resistance between metal and Si[3][4].

In this paper we will look at the relationship between the concentration of dissolved oxygen in ultrapure water used in wet processes and growth of native oxide. Outlines of ultrapure water removal of dissolved oxygen and other impurities will also be given and their basic functions discussed.

2. GROWTH OF NATIVE OXIDE IN ULTRAPURE WATER

Native oxide is classified in three different categories in which it is formed; 1) air 2) ultrapure water 3) chemical. In this paper, we will describe the native oxide formed in ultrapure water.

Figure 1 shows the time dependence of native oxide formed in room temperature when the dissolved oxygen concentration is changed. In this test, the thickness of native oxide is measured by XPS (X-ray Photoelectron Spectroscopy) and the average value is shown in the figure.

The wafer used in this test is n-Si(100) substrate (10^{15}/cm^3) which goes through H_2SO_4-H_2O_2 cleaning+ RCA cleaning and is processes with diluted HF, followed by 10-minute rinsing with ultrapure water. As shown in **figure 1**, although the native oxide grows further in accordance with the time, the growth rate of the native oxide is minimum when the dissolved oxygen concentration is smaller. This means that the growth of native oxide in ultrapure water depends on the dissolved oxygen concentration and that it is possible to effectively suppress its growth by reducing the dissolved oxygen concentration.

Figure 2 shows the measurments of the

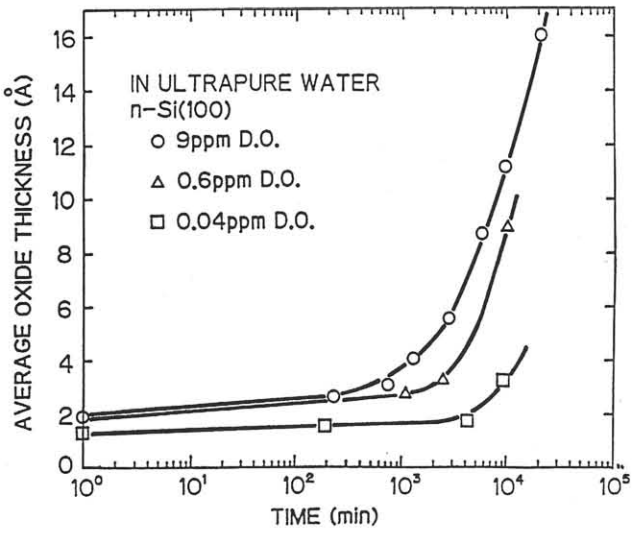
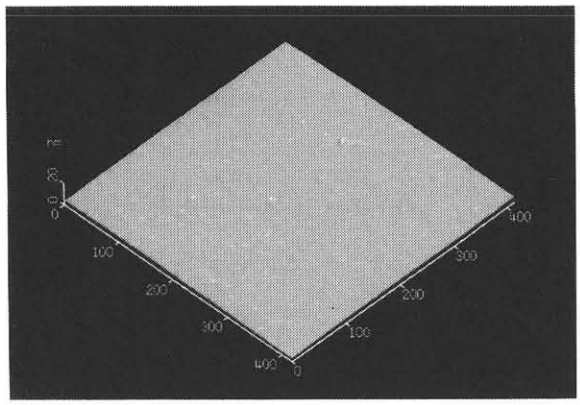
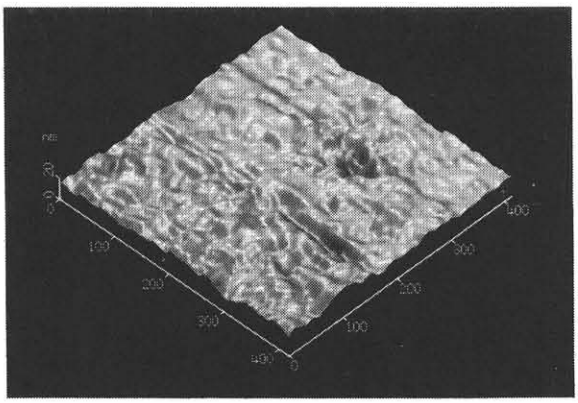


Fig.1 Oxide thickness as a function of immersion time of wafers in ultrapure water at room temperature for different dissolved oxygen concentrations



(a) 10-minute rinsing with Ultrapure Water



(b) Immersed in Ultrapure Water during 20 days

Fig.2 Surface conditions of a Si wafers measuring by STM

wafer surface immersed in ultrapure water, taken with a scanning tunneling microscope (STM), The concentration of dissolved oxygen in the ultrapure water in which the wafer was immersed was 9 ppm as in **Figure 1.** As is seen from **Figure 2-(b),** when a wafer is immersed in ultrapure water, the roughness of Si wafer surface increases with the lapse of time, reaching 100 A in **20** days of immersion.

The oxidation mechanism in ultrapure water is complex, however, and more detailed reseach will be necessary for the mechanism. Still, the discussion up to this point shows that native oxide necessarily grows when there is dissolved oxygen present in ultrapure water.[5)6)] However, the first step to suppress the native oxide is to remove as much dissolved oxygen as possible from the ultrapure water.

3. CONFIGURATION OF ULTRAPURE WATER SYSTEMS

The conventional ultrapure water systems are designed, aiming at the removal of impurities in water such as ions and particles.

As it has been found that native oxide grows when dissolved oxygen exsits and that it directly affects the device performance, it is required to develop a new ultrapure water system which is able to reduce dissolved oxygen as well as impurities in water to the ultimate level. The two ultrapure water systems installed in MiniSuper Cleanroom of Faculty of Engineering, Tohoku University based on this idea. Both systems are composed of not only the apparatuses to removal ions and organics in water such as Reverse Osmosis (RO), Ion Exchange, and Ultraviolet oxidation (UV), Ultrafiltration (UF), but also the two-step method to remove the dissolved oxygen.

Table 1 shows the water quality which currently obtained by the two ultrapure water systems. This is the water quality which has been stabilized after one-month operation. As shown in the table, all the analyzed table of impurities are close to the detection limit of analyzers, which proves that the purity of this ultrapure water is significantly high. In particular,the dissolved oxygen concentrations shown in the table are extremely low; 3-5 ppb for system 1 and 6-10 ppb for system 2.

4. DISSOLVED OXYGEN REMOVAL SYSTEM

As a method to reduce dissolved oxygen in water to extremely low level, two methods are presently being studied; 1) the hydrazine reduction method using catalyst resin 2) nitrogen gas bubbling method . Mehtod 1) is a chemical

Table 1 Quality of ultrapure water of new systems were recently installed in the mini-superclean room of Tohoku University

	RESISTIVITY (MΩ·cm)	TOC (μg/l)	SiO_2 (μg/l)	Dissolved Oxygen (μg/l)	TOTAL RESIDUE (μg/l)	PARTICLES (COUNTS /ml, >0.07μm)
SYSTEM 1	18.25	<1	<1	3-5	<1	1-2
SYSTEM 2	18.25	<1	<1	6-10	<1	1-2

Measurement equipment (maker)
*Resistivity meter : AQ-11 (D.K.K.)
*TOC meter : TOC-1000 (TOKIKO)
*Particle meter : K-LAMIC-100 (KURITA)
*DO meter : DOH-2 (D.K.K.)
*SiO2 meter : SLC-1605 (D.K.K.)
*Total Residue meter: HPM-1000 (Nomura Micro Science)

method to remove dissolved oxygen using reducing agent while method 2) is physical method to remove dissolved oxygen using oxygen partial pressure.

It is possible to remove the dissolved oxygen from ultrapure water directly using either of these methods, but the amount of chemicals and nitorogen gas required makes it desirable to remove some of the dissolved oxygen beforehand. The newly-installed systems apply the vacuum membrane degassing method to the first stage to remove dissolved oxygen.

4-1 VACUUM MEMBRANE DEGASSING METHOD

This method uses a gas-permeable membrane which permits quick permeation by oxygen, and dissolved oxygen in ultrapure water is removed by letting it permeate the membrane into a low pressure vapor phase.

Figure 3 shows the amount of residual dissolved oxygen when the pressure is changed, using an equipment with the module capacity of 70 liter. When the pressure level inside the module is reduced, the dissolved oxygen in water rapidly decreases. The figure also shows the theoretical amount of dissolved oxygen at each pressure level with the vapor pressure of water taken into account. The pressure level inside the equipment is now maintained at 50 Torr or less and the dissolved oxygen has been reduced to 300-400 ppb.

This vacuum degassing membrane method is considered as a very effective method to be applied at the first stage since this method enables such a compact apparatus to efficiently remove the dissolved oxygen.

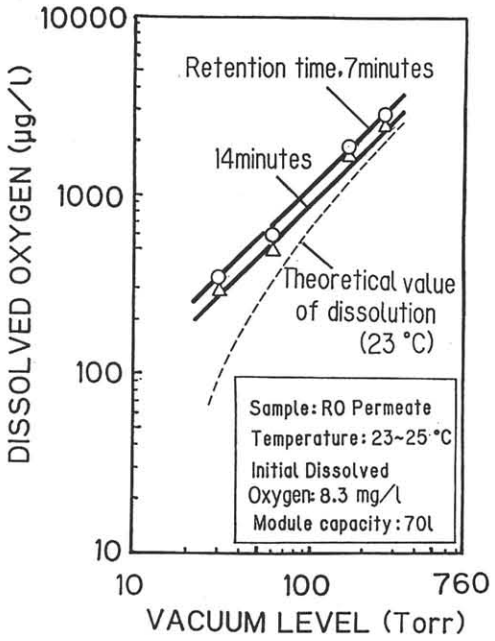


Fig.3 Relationship between the Dissolved Oxygen concentration and the vacuum level at varying retention time

4-2 REDUCTION METHOD WITH CATALYST RESIN

Applying the catalysis of palladium mounted on the surface of anion resin, the dissolved oxygen hydrazine (N_2H_4) or hydrogen (H_2) reacts with. As a result, the dissolved oxygen is decomposed into N_2 and H_2O in the former case, and into H_2O in the latter case.

It is theoretically possible for this method to completely remove the dissolved oxygen, provided that the appropriate amounts of dissolved oxygen and catalyst agent are reacted.

Figure 4 shows the relationship between the amount of residual dissolved oxygen and the amount of hydrazine injected into water, which went through the above-mentioned vacuum degassing through membrane. As shown in **Figure 4**, when N_2H_4 reducing agent of 1.0 mols is appropriately injected to the dissolved oxygen, it is possible to reduce the residual dissolved oxygen to 5 ppb or less.

4-3 NITROGEN GAS BUBBLING METHOD

This is a method to remove dissolved oxygen physically: a method to decrease the partial pressure of oxygen in water by having nitrogen gas to contact with fed water. The amount of dissolved oxygen in water versus partial pressure can be easily calculated with Henry's law.

In nitrogen gas bubbling system, water is supplied from the top of nitrogen gas bubbling tower, in which

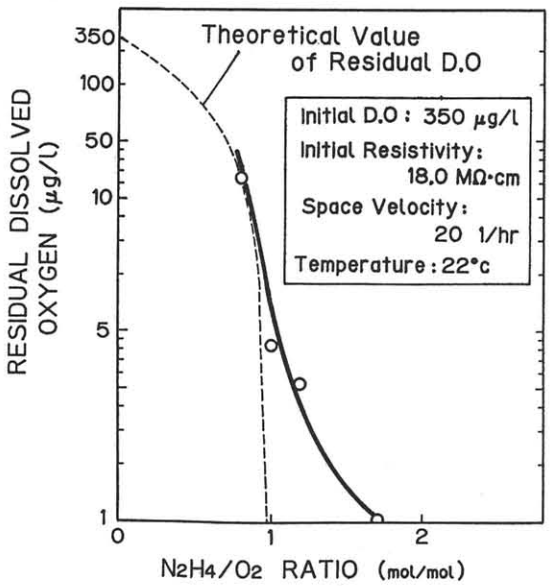


Fig.4 Relationship between Dissolved Oxygen concentration and the N_2H_4 per O_2 ratio at initial Dissolved Oxygen concentration is 350 ppb.

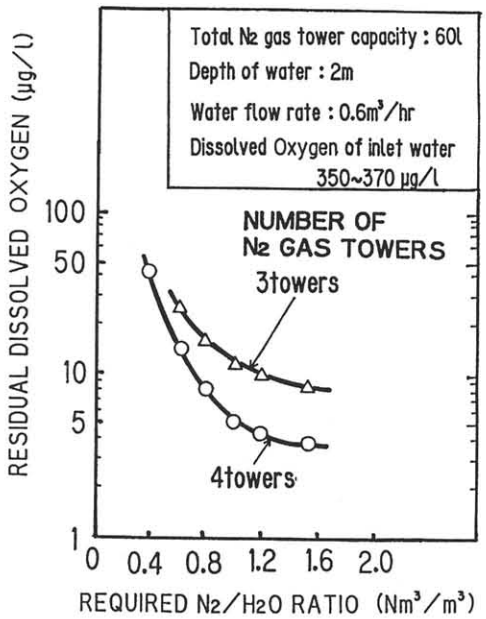


Fig.5 Relationship between the gas-liquid ratio and the residual Dissolved Oxygen concentration at different numbers of N_2 gas towers

water and fine bubbles of nitrogen gas are contacted in a counter-current manner. In order to inclease the contact efficiency, a multi-stage reaction system using 3-4 towers is applied to remove dissolved oxygen.

Figure 5 shows the relationship between the gas-liquid ratio and the residual dissolved oxygen concentration at different numbers of nitrogen gas towers. As shown in **Figure 5**, as the gas-liquid ratio and the number of towers are increased, the residual dissolved oxygen in water is gradually reduced. When the gas-liquid ratio is set at 0.8 and the number of towers is set at 4, it is possilble to limit the residual dissolved oxygen to 10 ppb or less.

5 SUMMARY

Native oxide grows on Si wafer when dissolved oxygen remains in ultrapure water. It is important to keep wafer from the atmosphere containig both moisture and oxygen in order to suppress the growth of native oxide. From this point, a new ultrapure water system using the two-stage dissolved oxygen removal method was developed, and this systems makes it possible to deliver ultrapure water with the dissolved oxygen of 10 ppb or less. Besides, this system is able to limit the amount ofimpurities such as TOC, Silica and Total-residue at the level of 1 ppb or less. The level of impurities in ultrapure water including dissolved oxygen, is getting close to the detection limit of analyzer.

Given the importance of wet processes to the production of ULSIs, it will be necessary to provide even better removal of impurities, including dissolved oxygen from ultrapure water in the future. At the same time, it will be important to further elucidate the growth mechanism for the native oxide that are formed on the surface of Si wafers.

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