Organic contaminants removal by oxygen ECR plasma

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Abstract

Recently electron cyclotron resonance (ECR) plasma have been explored for wafer cleaning applications, since it is known to do less damage to silicon surface than conventional plasma. Organic contaminants removal efficiency and plasma radiation damage of the ECR plasma cleaning have been investigated. In oxygen ECR plasma cleaning, the plasma exposure time needed to remove the organic contaminants on the silicon surface down to the detection limit is 40 s, but the one to reach the lowest surface roughness is 10 s. The leakage current level of the MOS capacitor made using the Si substrate exposed to oxygen ECR plasma for 40 s is 8×10^{-9} A. The optimum exposure time determined by considering the contaminants removal efficiency and the plasma radiation damage (or the leakage current level) is 40 s. Organic contaminants seem to be removed through both sputter-off mechanism by oxygen ion bombardment and evaporation mechanism by chemical reactions with excited oxygen atoms.
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1. Introduction

Wet chemical cleaning techniques based on RCA cleaning [1] have been widely used to remove contaminants on wafer surface. However, as devices are increasingly scaled down; the problems related to wet chemical cleaning become more serious [2]. Thus the need to develop dry cleaning technique which will replace wet chemical cleaning strongly exists for fabricating next generation devices. Plasma cleaning [3] is one of the most effective dry cleaning techniques in removing organic contaminants on silicon wafer surface. However, it also has a demerit of damaging the silicon surface which will result in leakage current in devices eventually [4,5]. Recently electron cyclotron resonance (ECR) plasma have been explored for wafer cleaning applications [6], since it is known to do less damage to silicon surface than conventional plasma. In our previous report [6] we compared just the removal efficiency of organic contaminants between UV/O$_3$ and oxygen ECR plasma cleaning and got to a conclusion that oxygen ECR plasma cleaning is more efficient in removing organic impurities than UV/O$_3$ cleaning. Nevertheless, the authors missed a very

important point in the paper. The authors did not consider the radiation damage caused by ECR plasma at all in the previous paper. Recently the authors realized two following things related to dry cleaning techniques:

(1) ECR plasma may cause plasma radiation damage on Si surface, which will induce leakage current in the devices fabricated on the Si substrate later although ECR plasma generally causes less radiation damage than ordinary plasma.
(2) A dry cleaning technique cannot be applied to mass production no matter how high the cleaning efficiency may be unless the leakage current induced by the cleaning technique is sufficiently low.

In this paper the optimum process condition of ECR plasma cleaning was determined by considering plasma radiation damage (or the current leakage) as well as impurity removal efficiency.

2. Experimental

The silicon wafers used in this study were p-type, B doped, Si(1 0 0), having dimensions of 50 mm × 10 mm × 3 mm. Prior to the intentional contamination, conventional cleaning

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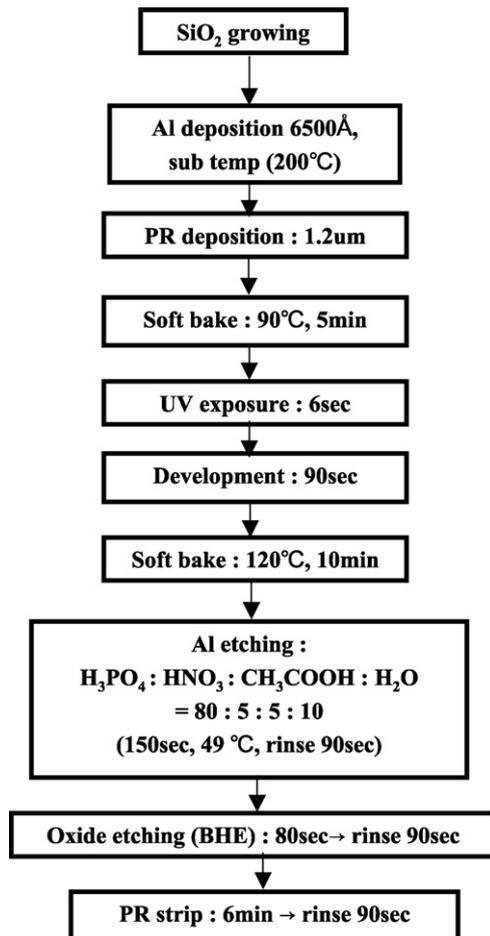Fig. 1. The process flow of fabricating MOS capacitors to measure the leakage currents.

transferred into the ECR plasma chamber. During the ECR plasma cleaning process the samples were positioned 20 cm below the center of the electromagnet. The base pressure of the ECR plasma chamber was 5×10^{-6} Torr, while the process pressure was approximately 5×10^{-3} Torr with an oxygen gas flow rate of 10 sccm. The microwave power was 300 W at a frequency of 2.45 GHz and the plasma chamber [6] had the form of a cylinder, made of stainless steel, with a diameter of 160 mm and a height of approximately 150 mm. The Si wafers were characterized by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FT-IR) (Nicolet 520 FT-IR spectrometer). The incident angle was $45°$, which resulted in 15 internal reflections [6]. Finally, the samples were characterized by atomic force microscopy (AFM) (Topomatrix Corporation: Accurex II).

The process flow for preparing MOS capacitor samples using as-contaminated and cleaned Si wafers to investigate their leakage currents is shown in Fig. 1. SiO$_2$ films 200 Å thick were grown by wet oxidation on Si wafers with a diameter of 8 in. Then, aluminum films 6500 Å thick were deposited by sputtering on the oxide. Test patterns with 102 MOS capacitors the SEM micrograph of which is shown in Fig. 2 were fabricated by using conventional lithography and wet chemical etching techniques. The area of each capacitor in the test patterns was 0.1 cm^2. Next, the I–V characteristic curves were obtained and the leakage currents were measured for the patterned samples as-deposited and treated with ECR plasma using an A-PM-90 wafer probe machine and an HP4145B device analysis system under the reverse bias of 0.5–1.0 V/s.

3. Results and discussion

Fig. 3 shows ATR-FT-IR spectra for the silicon wafers cleaning by oxygen ECR plasma with different ECR plasma exposure times. The absorption spectra resulting from organic contaminants are marked by several peaks with C–CH$_3$ at 2960 cm^{-1}, –CH$_2$– at 2930 cm^{-1}, –CH$_2$ at 2890 cm^{-1} and C–H

methods were used. Next, 20 ml of pure acetone was placed in a wafer storage box and the wafers were intentionally contaminated with contaminated acetone vapor in a clean hood for 3 h. The contaminated wafers were separately
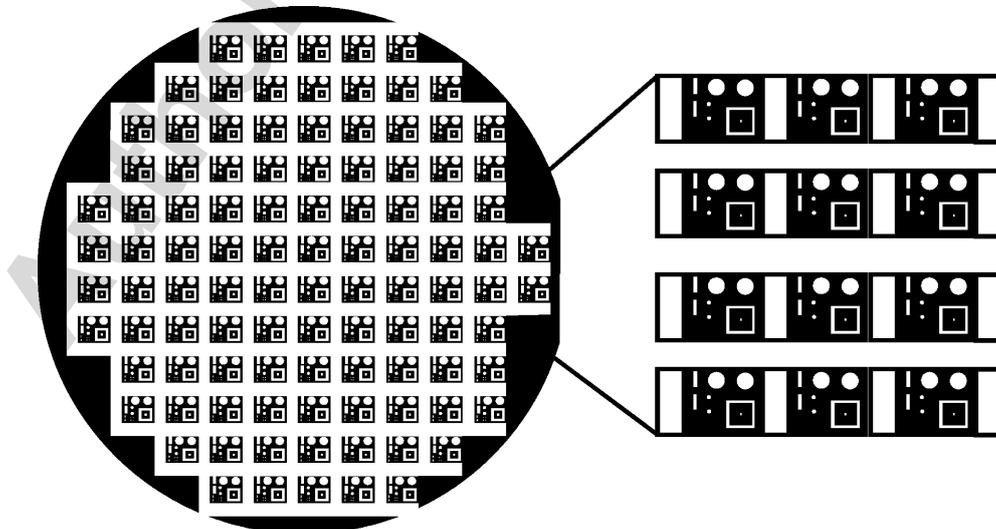

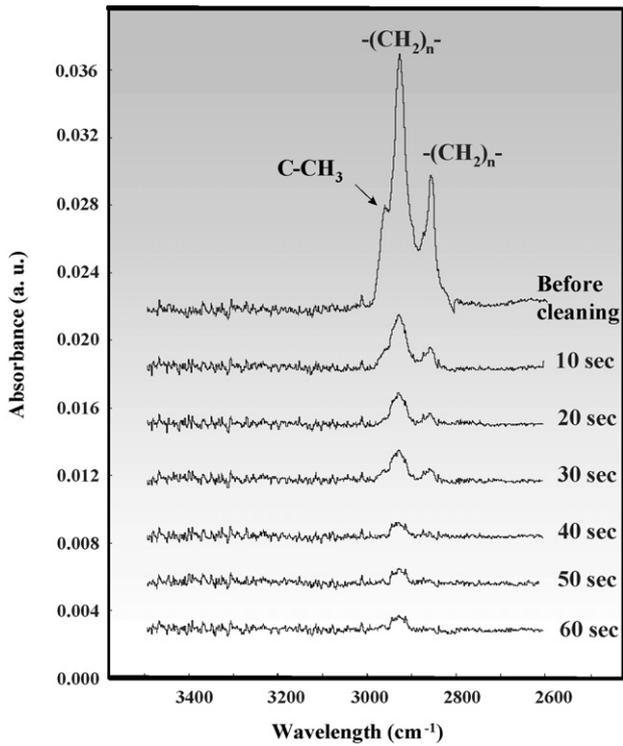Fig. 2. The test patterns for leakage current measurement.

Fig. 3. ATR-FT-IR spectra monitoring for O_2 ECR plasma removing process of organic contaminants on the silicon wafer surface.

stretching vibrations [–CH_3 and –$(CH_2)_n$–] at 2870 cm^{-1}. The intensity of the peak at 2930 cm^{-1} is maximum, implying the presence of –CH_2– stretching vibrations as a predominant group. The height of the highest peak decreases as the plasma

exposure time increases and stops decreasing at 40 s. It never decreases further with the exposure time, which suggests that it takes 40 s to remove the organic contaminants from the silicon sample surface down to the detection limit of the ATR-FT-IR analysis technique.

Fig. 4 is the AFM analysis results for silicon wafers at various stages of the oxygen ECR plasma cleaning. The root mean square (RMS) surface roughness decreases first and reaches minimum and then increases as the plasma exposure time increases. If we look at the AFM images carefully, we will see that the decrease in the RMS roughness during the time period of the first 10 s is attributed to the removal of the contaminants on the silicon surface, whereas the increase during the time period of the next 50 s is totally due to the mechanical damage on the silicon surface.

The AFM images show that voids form at the silicon wafer surface by the attack of energetic oxygen ions. Electronic excitation due to ion bombardment leads to the extraction of oxygen atoms. After this extraction some dangling bonds remain on the silicon surface. With subsequent ion bombardment the extracted O reacts with the dangling bonds and recreates the Si–O network. However, the network is deformed and strained in a metastable state. Si–O groups in the metastable areas are easily removed in comparison with those in other areas. This leads to the formation of voids at the silicon surface. Therefore, it is very important to determine the optimum plasma exposure time should be determined by trading off the two effects of the contaminants removal efficiency and plasma radiation damage.

Considering the ATR-FT-IR and AFM analysis results together we may conclude that the optimum process time falls
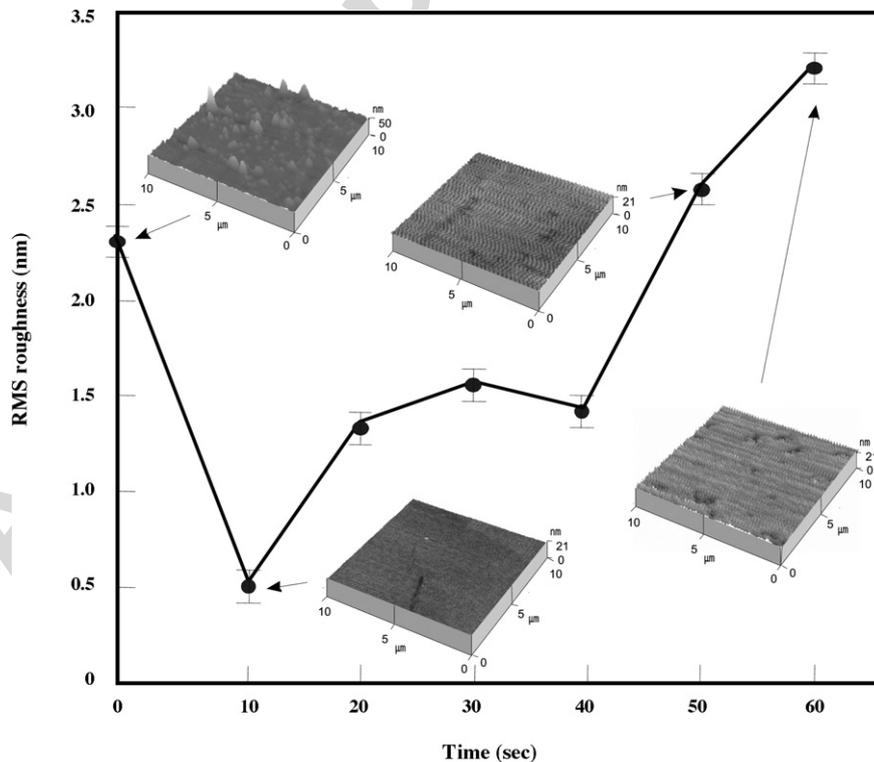

Fig. 4. Surface roughness after O_2 ECR plasma cleaning process for removing organic contaminants as a function of the cleaning time.
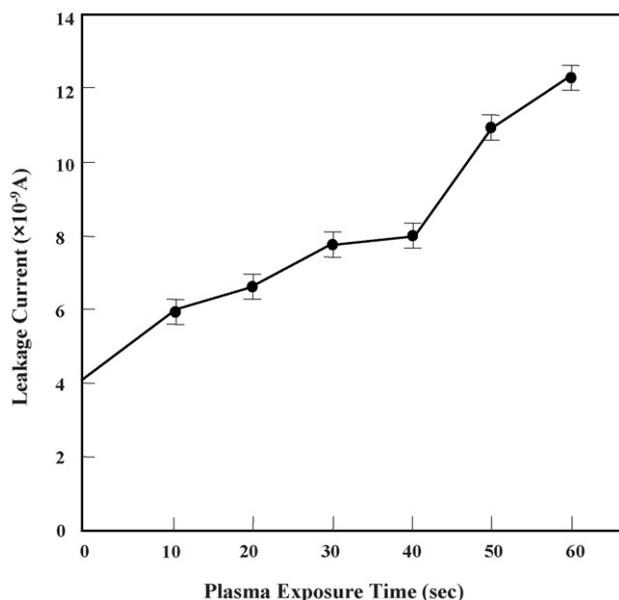
Fig. 5. MOS capacitor leakage current as a function of the plasma exposure time in the oxygen ECR plasma cleaning.

Fig. 6. ATR-FT-IR spectra monitoring for H_2 ECR plasma removing process of organic contaminants on the silicon wafer surface.

in the range from 10 to 40 s. We made capacitors on the silicon wafers with the ECR plasma cleaning treatment to measure leakage currents caused by the plasma radiation damage for different plasma exposure times. Fig. 5 shows that the leakage current of the capacitor increases as the plasma exposure time in ECR plasma cleaning increases. The leakage current level for the exposure times of 10–40 s falls in the range of $(6-8) \times 10^{-9}$ A per chip (where chip means a capacitor with an area of 0.1 cm^2 in a test pattern), which is not so high to accept for giga Dynamic Random Access Memorys (DRAMs). The acceptable leakage current level for 2 GB DRAM which is a device of state of the art these days is about 1×10^{-9} A/cm^2 [7]. Therefore, it seems to be desirable to go up to the process time of 40 s to remove the organic contaminants completely. In other words, we may conclude that the optimum process time for organic contaminants removal is 40 s.

Hydrogen ECR cleaning was also conducted for the silicon samples to compare its contaminants removal efficiency with that of oxygen ECR cleaning. The ATR-FT-IR and AFM analysis results for it are shown in Figs. 6 and 7, respectively. The height of the main peak in the ATR-FT-IR spectra in Fig. 6 decreased quite a bit for the first 10 s as the plasma exposure time increased but further decrease did not nearly occur after that with an increase in the exposure time. Even after the exposure time of 5 min the peak is far higher than the detection limit of the ATR-FT-IR analysis. The hydrogen ECR plasma cleaning does not seem to be effective enough to remove the organic contaminants on silicon surface although the AFM analysis results in Fig. 7 show that the hydrogen ECR plasma cleaning has no difficulty in removing organic contaminants. According to AFM images of Fig. 7 most contaminants seems to have been removed after the silicon sample surface was exposed to hydrogen ECR plasma for 5 min, but very thin film-type organic contaminants were detected by AFM.
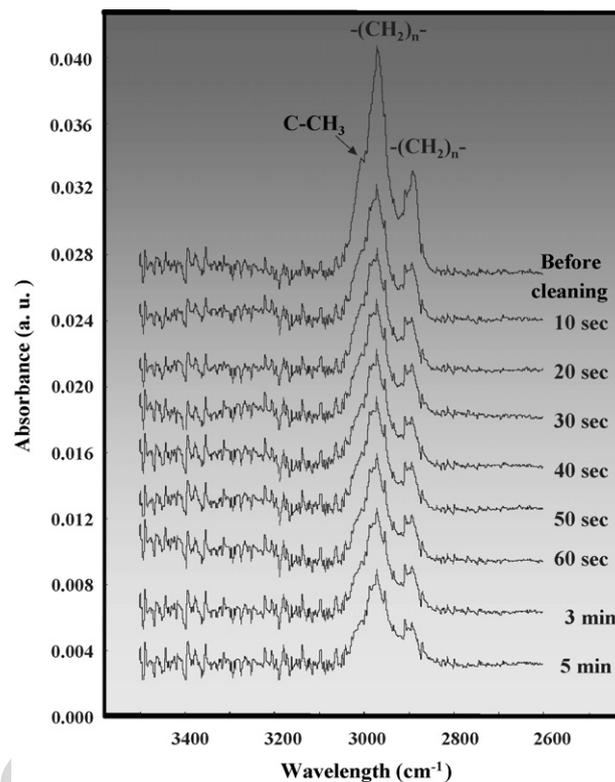
On the basis of the above experimental results, we propose the following mechanism for organic contaminants removal of ECR plasma cleaning. We can think of three different mechanisms [2]: lift-off mechanism, sputter-off mechanism, and evaporation mechanism. In the case of oxygen ECR plasma cleaning organic contaminants are removed primarily by sputter-off mechanism and secondarily by evaporation mechanism, but lift-off mechanism seems to make nearly no contribution. In general sputter-off mechanism is dominant in the case of plasma cleaning using a plasma with a large ion mass such as oxygen plasma because of its high ion energy. However, evaporation mechanism also plays a role of removing organic impurities to some extent because organic materials react with oxygen chemically.

In contrast, in the case of hydrogen ECR plasma cleaning organic contaminants are removed mostly by lift-off mechanism, but the other two mechanisms do not nearly seem to contribute.

First, let us think about sputter-off mechanism. To remove organic contaminants ($C_x H_y O_z$), C–Si, H–Si and O–Si bonds must be broken. In other words the threshold ion energy is the same as the largest value of the bond strength for C–Si, H–Si and O–Si. In order to break these bonds the ion energy must be larger than these bond strengths. The bond strength values for these bonds are given in Table 1. The ion energy is higher near the exhaust and lower near the microwave window in an ECR plasma chamber. If we calculate the oxygen ion energy at 0.75×10^{-3} Torr, the value falls in the range form 1446 to 3470.4 kJ/mol. This energy is large enough to break C–Si, H–Si
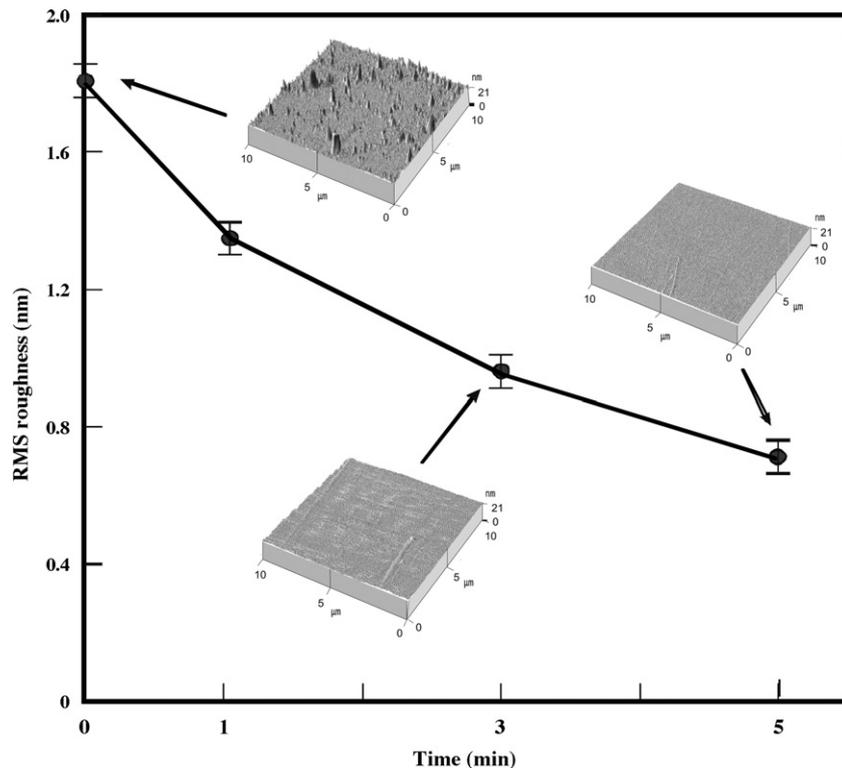
Fig. 7. Surface roughness after H_2 ECR plasma cleaning process for removing organic contaminants as a function of the cleaning time.

Table 1
Binding energies

Bond	Binding energy	
	(kcal/mol)	(kJ/mol)
C–Si	104 ± 5	435 ± 21
O–Si	190.9 ± 2	798.7 ± 8.4
H–Si	71.34 ± 0.11	298.49 ± 0.46

and O–Si bond (Table 1). Therefore, the energetic oxygen ions are capable of removing these organic contaminants directly form the silicon surface at the operating pressure of 5×10^{-3} Torr. On the other hand, in the case of hydrogen ECR plasma cleaning the hydrogen energy at 0.75×10^{-3} Torr is calculated to be in the range from 90 to 217 kJ/mol. This energy is too small to break C–Si, H–Si and O–Si bonds. Therefore, the hydrogen ions are not capable of removing organic contaminants directly. Next, let us think about evaporation mechanism. Neutral oxygen atoms in oxygen ECR plasma react with organic contaminants to form volatile molecules such as CO_2, CO, H_2O, O_2, H_2, whereas neutral hydrogen atoms in hydrogen ECR plasma do not react with organic contaminants to form volatile molecules. Thirdly, let us think about lift-off mechanism. In this mechanism organic contaminants are indirectly removed by being swept away when the underlaying native oxide layer or the silicon atoms at the silicon substrate surface are removed. Native oxides and silicon atoms at the silicon substrate surface can be removed by chemical reaction with neutral hydrogen or oxygen ion bombardment. This mechanism seems to be the only one relevant to hydrogen ECR plasma cleaning.

4. Conclusion

Organic contaminants removal efficiency and plasma radiation damage of ECR plasma cleaning have been investigated. In oxygen ECR plasma cleaning, the plasma exposure time needed to remove the organic contaminants on the silicon surface down to the detection limit is 40 s, but the one to reach the lowest surface roughness is 10 s. The leakage current level of the MOS capacitor made using the Si substrate exposed to oxygen ECR plasma for 40 s is 8×10^{-9} A, which is not so high to accept for the current memory devices such as 2 GB DRAM. The optimum exposure time determined by considering the contaminants removal efficiency and the plasma radiation damage (or the leakage current level) is 40 s.

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