

Evaluation of the removal efficiency of organic impurities by ECR plasma based on the ATR-FTIR analysis

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The removal efficiencies of organic impurities existing on the surface of silicon wafers by O₂, H₂, and N₂O ECR plasma cleaning techniques were compared based on the Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) analysis results. It was found that oxygen ECR plasma was the most efficient and hydrogen ECR plasma was the least efficient in removing organic impurities on Si wafers. In ECR oxygen plasma cleaning, the plasma exposure time to reach the detection limit of ATR-FTIR was 40s. Also the contaminants removal mechanism in O₂, H₂, and N₂O ECR plasma cleaning have been discussed.

Key words: Dry cleaning, Organic contaminant, Oxygen plasma, Hydrogen plasma, N₂O plasma ATR-FTIR

1. INTRODUCTION

As the device geometries based on silicon wafers continue to shrink, trace amount of volatile organic contaminants adsorbed by silicon surface are found to have increasingly detrimental impact on the product performance and yield such as degradation of gate-oxide integrity (GDI) and deviation in the thickness of CVD films [1]. Organic pickup during integrated circuits (IC) fabricating processes is hard to avoid. It has been shown that the residual organic contaminants on silicon wafer surfaces are not only a result of absorption of organic volatiles in the air but also the organic additives outgassed from wafer storage boxes, which are usually made of polypropylene or polycarbonate materials [2]. It has been also found that the absorbance of organic compounds from enclosure increases monotonically as a function of wafer storage time. Among the dry cleaning techniques, the most effective ones for removing organic contaminants are UV cleaning and plasma enhanced cleaning. Recently, magnetically confined microwave or electron cyclotron resonance (ECR) plasmas have been used for wafer cleaning [3-4]. Compared with conventional plasma systems, the electron cyclotron resonance (ECR) plasma system can deliver a higher density of low energy ions to the substrate without sacrificing cleaning efficiency.

In this paper the removal efficiencies of O₂, N₂O, H₂ ECR plasma cleaning for organic contaminants on silicon wafers have been investigated based on Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) analyses.

2. EXPERIMENTAL

The silicon wafers used in this study were *p*-type, B-doped, Si(100) with a resistivity of 5-10 Ω-cm. Prior to the intentional contamination, conventional cleaning methods were used. The wafers were pre-cleaned with a piranha solution (H₂SO₄:H₂O₂ = 4:1) for 10 min at 120 °C to remove organic and particulate contaminants on the Si wafer surfaces and with a HF solution (HF: deionized water = 1:10) for 1 s at room temperature to eliminate

native oxides in order to establish a reproducible starting surface condition. After this treatment the samples were rinsed in deionized water for 5 min and then dried by blowing N₂. Then, 20 ml of pure acetone (Duk San pure chemical Co. Ltd.) was placed in a plastic wafer carrier box (Entegis Inc.) and the wafers were intentionally contaminated with acetone vapors in a clean hood for 3 hr. The contaminated wafers were transferred into the ECR plasma chamber. 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 or hydrogen gas flow of 10 sccm or an N₂O flow rate of 15 sccm. The flow rate of each gas has been optimized from the viewpoint of cleaning efficiency through our preliminary experiments. The microwave power was 300W at a frequency of 2.45 GHz, and the plasma chamber made of stainless steel had a cylindrical form, with a diameter of 160 mm and a height of approximately 150 mm [4]. The Si wafers were characterized by ATR-FTIR (Nicolet 520 FTIR spectrometer). The incident angle was 45 °, which resulted in 15 internal reflections [4].

3. RESULTS AND DISCUSSION

Fig. 1 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-CH₃ at 2960 cm⁻¹, -CH₂- at 2930 cm⁻¹, -CH₂ at 2890 cm⁻¹ and C-H stretching vibrations [-CH₃ and -(CH₂)_n-] at 2870 cm⁻¹ [5]. The intensity of the peak at 2930 cm⁻¹ is maximum, implying the presence of -CH₂- 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.

Hydrogen ECR cleaning was also conducted for the

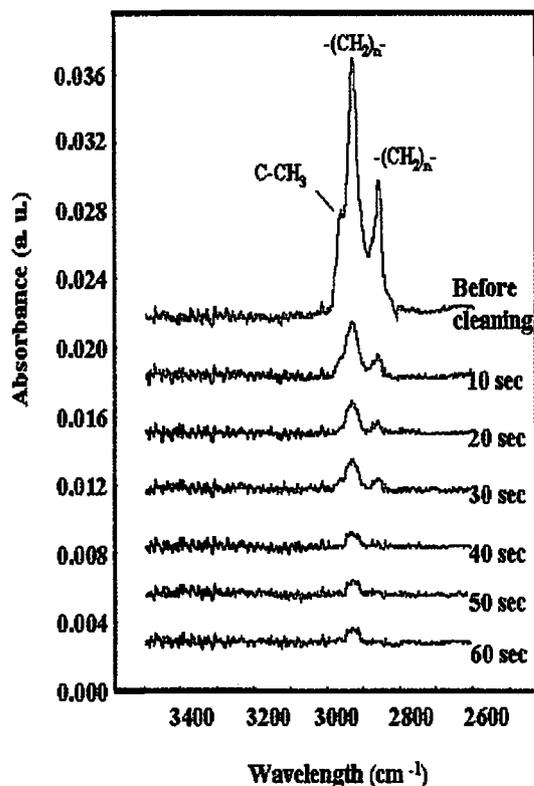


Fig. 1. ATR-FT-IR spectra monitoring for O₂ ECR plasma removing process of organic contaminants on the silicon wafer surface.

silicon samples to compare its contaminants removal efficiency with that of oxygen ECR cleaning. The ATR-FT-IR analysis results for it are shown in Fig. 2. The height of the main peak in the ATR-FT-IR spectra in Fig. 2 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.

Organic contaminants [6] desorbed from polypropylene storage boxes are mainly 2,6-di-*t*-butyl-2,5-cyclohexadiene-1,4-dione, dibutyl phthalate (DBP) and 2,6-di-*t*-butyl-4-methyl-phenol (BHT). In general, a silicon wafer surface shows strong polarity effects and, therefore, is suitable for attracting organic additives containing polar groups [7]. As a result, organic contaminants that have relatively low vapor pressures, small molecular weights and polar groups, such as a >C=O and O-H, can be easily adsorbed by the native oxides on the silicon surface. To remove these organic contaminants (C_xH_yO_z), C-Si, H-Si and O-Si bonds must be broken. That means that the threshold ion energy should be the same as the largest value of the bond strength for C-Si, H-Si and O-Si.

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 [8]: lift-off mechanism, sputter-off mechanism, and evaporation

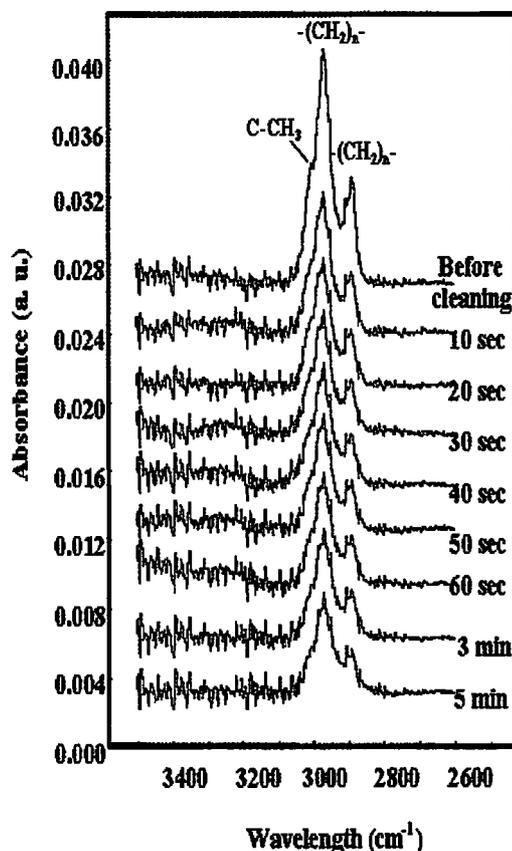


Fig. 2. ATR-FT-IR spectra monitoring for H₂ ECR plasma removing process of organic contaminants on the silicon wafer surface

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. It is well known that hydrogen plasma is a gaseous and electrically neutral state containing electrons, ions, neutral atoms and molecules.

When exposed to the H₂ plasma, the Si wafer surface produces volatile compounds due to the chemical reaction with the plasma constituents and is etched. Because of the fact that excited hydrogen atoms generated in H₂ plasma have relatively small molecular weights and low energies, organic contaminants cannot be easily removed by sputter-off. It is reported [9] that the hydrogen ion bombardment (sputter-off) has hardly an influence on the etching of silicon oxides. Therefore, it is likely that the cleaning mechanism is not sputter-off, but lift-off following the chemical reaction between the chemically reactive species and organic contaminants. The details of the mechanism are

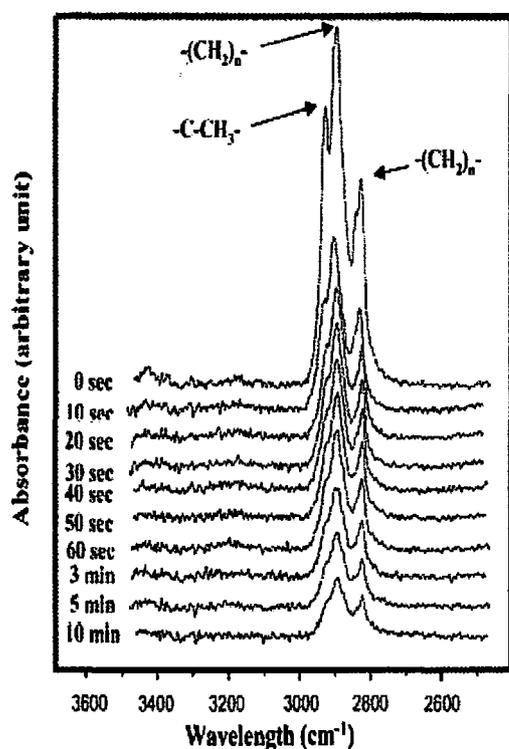


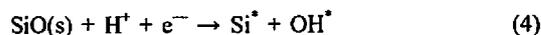
Fig. 3. ATR-FTIR spectra of the Si wafer surface after N_2O ECR plasma cleaning with different times.

proposed as follow [10]:

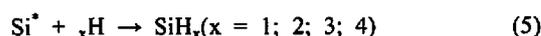
After generating the hydrogen plasma, electron and ion impact processes will be the sources of excitation in certain plasma discharges. These processes can be written in the following steps:



Here the symbols of H° , H^{\bullet} , H^+ and e^{-} represent neutral hydrogen, hydrogen radical, hydrogen ion and electron, respectively. These species play important roles in the removal of chemicals and native oxides from the silicon surface. It is previously reported [11-13] that the SiO_2 layer gets easily removed by the remote plasma H_2 cleaning process. Oxide etching may occur via a hydrogen ion assisted mechanism through the following reactions:



After a native oxide film on silicon wafer is etched, a silicon substrate is continuously etched by hydrogen species and a very volatile SiH_4 gas is generated as in the following reaction.



The organic contaminants are also eliminated

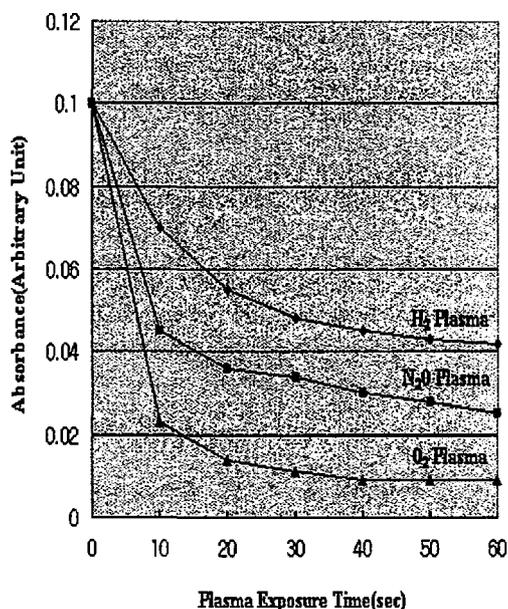
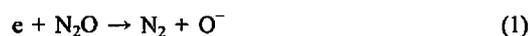


Fig. 4. Change of the absorbance for the C- CH_3 group in ATR-FTIR spectra with the plasma exposure time.

together with the SiH_4 gas when a SiH_4 gas is desorbed. Finally, considering the chemical reaction between the chemically reactive species and organic contaminants in H_2 plasma cleaning, it seems that the reaction hardly occurs. In other words, the reaction between organic contaminants and hydrogen ion can not occur spontaneously at the plasma cleaning process temperature. It is not a spontaneous reaction from the viewpoint of thermodynamics. Therefore, the removal mechanism of organic impurities can be considered to be a lift-of the organic impurities during the removal of the underlying chemical oxides subjected to the ECR H_2 plasma treatment.

On the other hand when Si wafer surfaces are exposed to an N_2O plasma, organic contaminants are usually sputtered off from the surface because of the bombardment of energetic ions. In general the energy of an ion is proportional to the mass of the ion. The energy of N_2O ion is far higher than that of H ion because the ratio of the molecular mass of N_2O to the atomic mass of H is 22:1. Therefore, sputtering mechanism is dominant in N_2O plasma cleaning. On the other hand an N_2O ECR plasma acts as a prolific oxidizer. The main positive and negative ions formed by the bombardment of electrons with N_2O atom are N_2O^+ and O^- . Formation of a negative ion is followed by the formation of NO^- , which in turn can lead to electron detachment, as summarized by the following reactions [8].



The production of abundant O^- leads to oxidation of the organic compounds and subsequently decomposition takes place into H_2O , O_2 , H_2 , CO , and CO_2 all of which have high vapor pressures (lift off).

4. CONCLUSIONS

Among three different kinds of ECR plasma cleaning oxygen ECR plasma cleaning is the most efficient, N_2O ECR plasma cleaning the next, and hydrogen ECR plasma cleaning the least efficient in removing organic impurities on Si wafer surfaces. The optimum oxygen ECR plasma exposure time is 40 s.

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