Organic contaminants removal by N$_2$O plasma treatment

DAE KYU KIM, YUN KYU PARK, CHONGMU LEE*
Department of Materials Science and Engineering Inha University, 253 Younghyeon-dong, Incheon 402-751, Korea
E-mail: cmlee@inha.ac.kr

Contamination of Si surfaces by organic species significantly deteriorates the reliability of semiconductor device performance in ultra-large-scaled integrated circuits (ULSIs) [1, 2]. A trace amount of organic contaminants on silicon wafer surfaces have an increasingly detrimental impact on the performance and the yield of a semiconductor device with highly reduced dimensions, such as degradation of gate-oxide integrity (GOI) [3–5] and deviation in the thicknesses of CVD films. 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 [6] but also the organic additives outgassed from wafer storage boxes, which are usually made of polypropylene or polycarbonate materials [7]. It has been also found that the absorbance of organic compounds from enclosure increases monotonically as a function of wafer storage time [8].

Conventionally, wet cleaning, particularly RCA cleaning is quite efficient in removing most organic contaminants [7]. However, as the devices get increasingly scaled down, the critical size of particles allowed is reduced, thereby enhancing the adhesion between the particles and the substrate, and the possibility of redeposition of removed particles [9]. This has made the solvent-based cleaning process more inefficient in removing the microparticles from microelectronic devices. Among the dry cleaning techniques, the most effective ones for removing organic contaminants are UV cleaning and plasma enhanced cleaning. It is worth noting that UV/O$_3$ cleaning causes less radiation damage and is more controllable [10]. Recently, magnetically confined microwave or electron cyclotron resonance (ECR) plasmas have been used for wafer cleaning [11, 12]. 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 efficiency of N$_2$O ECR plasma cleaning for organic contaminants on silicon wafers, stored in plastic boxes, has been studied.

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 precleaned with a piranha solution (H$_2$SO$_4$:H$_2$O$_2$ = 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 N$_2$. 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 8.63 × 10^{-6} Torr, while the process pressure was approximately 6.7 × 10^{-3} Torr with an N$_2$O flow rate of 15 sccm. The microwave power was 300 W 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 [12]. The Si wafers were characterized by ATR-FTIR (Nicolet 520 FTIR spectrometer). The incident angle was 45°, which resulted in 15 internal reflections [12].

Fig. 1 shows ATR-FTIR spectra for the silicon wafers cleaned by an N$_2$O ECR plasma with different exposure times up to 10 min. The absorption spectra resulting from the organic contaminants are marked by several peaks, with C—CH$_3$ at a wavelength of 2960 cm^{-1}, —CH$_2$— at 2930 cm^{-1}, —CH at 2890 cm^{-1} and C—H stretching vibrations [—CH$_3$ and —(CH$_2$)$_n$—] at 2870 cm^{-1} The peak at 2930 cm^{-1} has a maximum inteasity, implying the presence of —CH— stretching vibrations as a predominant group [13]. In Figs 2–4, it is very much evident that intensities of C–CH$_3$ and —(CH$_2$)$_n$— bands decrease sharply within the exposure time of 10 s and a substantial cleanliness has been achieved after 60 s, thereafter the contaminant concentrations gradually decreases with the plasma exposure time.

Organic contaminants [14] 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. As a result, organic contaminants that have relatively low vapor pressures, small molecular weights and polar groups, such as a >C=O and —OH, can be easily adsorbed by the
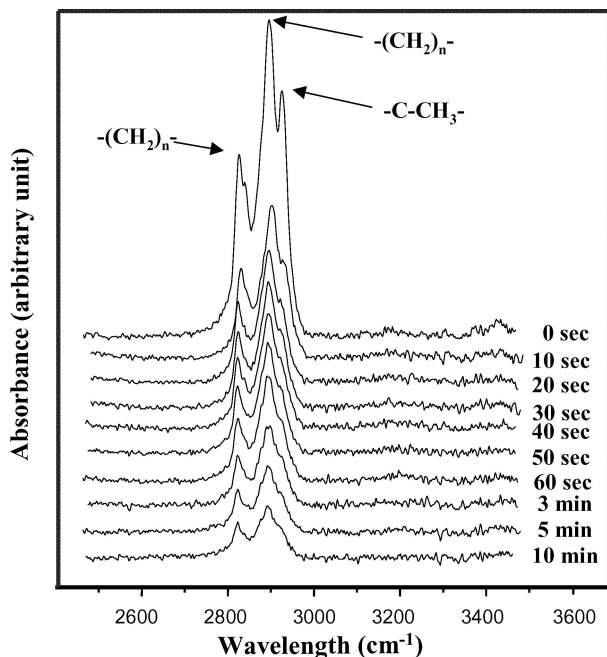
Figure 1 ATR-FTIR spectra of the Si wafer surface after N_2O ECR plasma cleaning with different times.
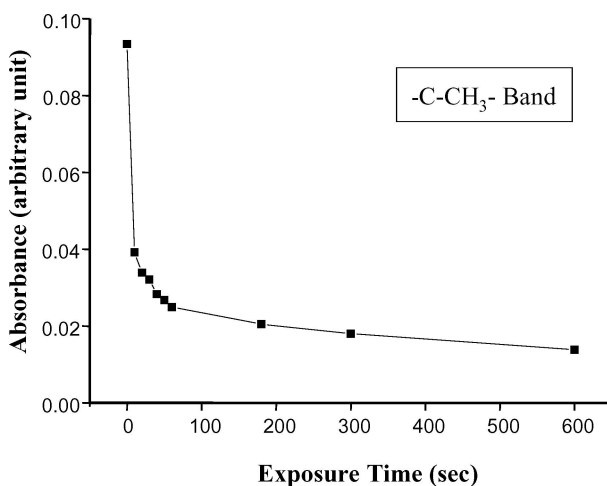

Figure 2 Change of the absorbance for the C-CH$_3$ group in ATR-FTIR spectra with the plasma exposure time.
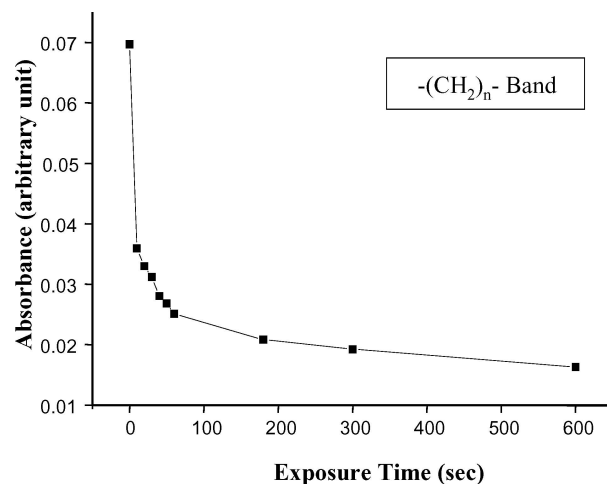

Figure 3 Change of the absorbance for the $-(CH_2)_n-$ group in ATR-FTIR spectra with the plasma exposure time.
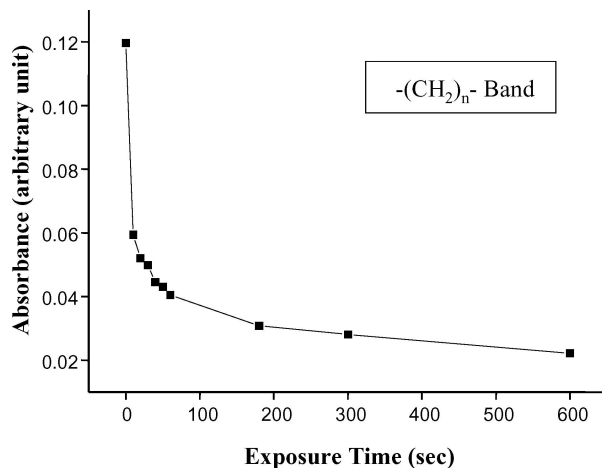

Figure 4 Change of the absorbance for the $-(CH_2)_n-$ group in ATR-FTIR spectra with the plasma exposure time.

native oxides on the silicon surface. To remove these organic contaminants ($C_x H_y O_z$), 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. In order to break these bonds the ion energy must be sufficiently larger than the bond strength. The values of bond strengths are given in Table I. The ion energy is higher near the exhaust and lower near the microwave window in the ECR plasma chamber. If we calculate the ion energy at 6.7×10^{-3} Torr, the value is in a range of 1446–3470.4 KJ/mol from the ion energy distribution [15]. This energy is sufficiently large to break C$-$Si, H$-$Si and O$-$Si bonds (Table I). Therefore, the energetic ions are capable of removing these organic contaminants from the silicon surface at an operating pressure of 6.7×10^{-3} Torr.

It is well-known that an N_2O plasma is in an electrically neutral state containing electrons, ions, atoms and molecules. 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. 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 [16].
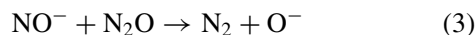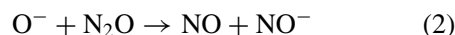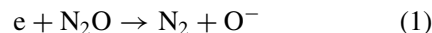
$$e + N_2O \rightarrow N_2 + O^- \qquad (1)$$

$$O^- + N_2O \rightarrow NO + NO^- \qquad (2)$$

$$NO^- + N_2O \rightarrow N_2 + O^- \qquad (3)$$

TABLE I The binding energies for C$-$Si, H$-$Si and O$-$Si bonds

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

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).

A dry cleaning technique using an N_2O ECR plasma was applied to silicon (100) wafers for the removal of organics, intentionally contaminated on the silicon surface. Interestingly a noticeable change was observed in the concentration of contaminants after plasma exposure for only 10 s. The organic contaminants can be substantially reduced by this technique with an appropriate exposure time. An N_2O ECR plasma removes organic contaminants from silicon surfaces by oxidizing them and then decomposing the oxides into volatile compounds such as H_2O, O_2, H_2, CO, and CO_2.

References

1. K. SAGA and T. HATTORI, *Appl. Phys. Lett.* **71** (1997) 3670.
2. T. OGATA *et al.*, *Jpn. J. Appl. Phys.* Part 1 **37** (1998) 2468.
3. T. YOSHIDA, D. IMAFUKU, S. MIYAZAKI and M. HIROSE, in Proceedings of the 3rd International Symposium on Ultra Clean Processing of Silicon Surfaces, UCPSS '96, Acco, Leuven, Belgium, 1996, p. 305.
4. F. TARDIF, G. QUAGLIOTTI, T. BAFFERT and L. SECOURGEON, in Proceedings of the 3rd International Symposium on Ultra Clean Processing of Silicon Surfaces, UCPSS '96, Acco, Leuven, Belgium, 1996, p. 309.
5. T. OHMI, *J. Vac. Sci. Technol.* A **13** (1995) 1665.
6. A. J. MULLER, L. A. PSOTA-KELTY, J. D. SINCLAIR and W. MORRISON, in "Semiconductor Cleaning Technology/1989," edited by J. Ruzyllo and R. E. Novak (The Electro-chemical Society, Pennington, NJ, 1989) PV90-9, p. 204.
7. W. KERN and D. A. PUOTINE, *RCA Rev.* **31** (1970) 187.
8. W. VANDERVORST, H. BENDER, W, STORM, M. HEYNS *et al.*, *Microelectron. Eng.* **28** (1995) 27.
9. T. AHN and H. JEON, *J. Korean Phys. Soc.* **30** (1997) S252.
10. Y. HARA, T. YAMAZAKI, T. SUGII, R. SUGINO, T. ITO and H. ISHIKAWA, *SPIE* **797** (1987) 90.
11. H.-W. KIM and R. REIF, *Thin Solid Films* **289** (1996) 192.
12. K. CHOI, T.-J. EOM and C. LEE, *ibid.* **435** (2003) 227.
13. K. CHOI and C. LEE, *J. Korean Phys. Soc.* **42** (2003) S703.
14. W. LEE and H. JEON, *J. Korean Phys. Soc.* **30** (1997) S307.
15. J. CHEN and Z. REN, *Vaccum* **52** (1999) 411.
16. D. A. PARKS, *J. Chem. Soc. Faraday Trans.* II **68** (1972) 2103.