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Effect of Organic Compounds on Gate Oxide Reliability

Yoshimi SHIRAMIZU and Hiroshi KITAJIMA

ULSI Device Development Laboratories, NEC Corporation,
1120 Shimokuzawa, Sagamihara, Kanagawa 229, Japan

The correlation between the type of organic contaminants and the degradation of gate oxide films was studied. It was found that the thermal stability of organic compounds on silicon substrate surface depends on their structure. Organic compounds, which are benzenoid, were found to be the cause of the reliability deterioration of gate oxide films, because these organic compounds can hardly be removed from silicon surface by heat treatment only.

1. Introduction

Metal contaminants have been reduced in ULSI device manufacturing. One reason is that metal contamination on silicon substrate can be quantified sensitively using chemical analysis techniques such as Vapor Phase Decomposition Atomic Absorption Spectrometry (VPD-AAS) (1). The other reason is that they have serious effects on the dielectric breakdown degradation of gate oxide films, p-n junction leakage currents and crystalline defect generation (2).

Organic materials have been thought to be easily decomposed and desorbed from silicon surface during heat treatment. However, it was recently reported that organic compounds cause the dielectric breakdown of gate oxide films (3)(4).

In this paper, the correlation between the type of organic contaminants and the reliability degradation of gate oxide films is reported. The thermal stability of organic compounds on the silicon substrate surface is also clarified to evaluate structural changes during the oxidation process(5).

2. Experimental

Photoresist was coated on the surface of P-doped (4-6 Ω cm <100>) silicon substrates after RCA cleaning. Photoresist films were then exposed to Ultra Violet light and developed using an alkaline solution, and finally a heat treatment was carried out at 130 ℃ for 30 minutes. Three resist ashing methods were compared with regard to the removal efficiency of organic compounds.

Organic compounds on the silicon substrate surface were quantified using Thermal Desorption Spectroscopy Gas Chromatography Mass Spectrometry (TDS-GC-MS). Metal impurities on silicon substrate surface after several wet processes were also analyzed by using VPD-AAS.

The gate oxide film reliability was evaluated by measuring Time Dependent Dielectric Breakdown (TDDB) and the gate oxide breakdown voltage.

Heat treatment of silicon substrates contaminated with Dioctyl Phthalate (DOP) was carried out at 400, 650 or 950 ℃ for 5 minutes in N_2/O_2. The surface concentration of DOP is controlled by exposing time of wafer to DOP vapor. The decomposition and desorption of DOP on the silicon substrate surface was evaluated by Fourier Transform Infrared Spectrometry Alternated Total Reflection (FTIR-ATR using Ge prism) and X-ray Photoelectron Spectroscopy (XPS).

3. Results and discussion

3-1 Analysis of organic compounds

Figure 1 shows the concentration of organic compounds remaining on the silicon substrate surface after each resist ashing method. Organic compounds A, B and C come from decomposed photoresist films. Organic compounds D is phthalic anhydride, its source is wafer boxes. The silicon substrates used for the TDS-GC-MS analysis were kept for several days in a wafer box made of plastic materials. The amount of organic compound D in MOS devices shown in Figure 2 is assumed to be much smaller than on the wafer for analysis. Organic compound A is benzenoid including C=O bond. Organic compound B is benzenoid. Organic compound C is cyclo-ether, not benzenoid and not having C=C bond. Organic compounds

A and B could hardly be removed by wet ashing (H_2SO_4 / H_2O_2) only.

3-2 Reliability of gate oxide films

Figure 2 shows the cumulative TDDB failure rate for the gate oxide films after the three different ashing methods. The TDDB failure rate is the largest for gate oxide films treated by wet ashing only. The TDDB characteristics are similar for the two other ashing methods. Figure 3 shows frequency versus gate oxide breakdown voltage relation which is affected by the three different ashing methods. A mode and B mode failures are observed in the dielectric breakdown characteristics of the gate oxide films after only wet ashing. The gate oxide films after two other ashing methods show the intrinsic dielectric breakdown (C mode failure).

Figure 4 shows that metal impurities on silicon substrate surface after only wet ashing and wet ashing + wet cleaning. Metal impurities on silicon substrate surface after two ashing methods are lower than 4×10^{10} atoms/cm^2, and metal contaminants in this level have little effect on the gate oxide reliability.

It is clarified by comparing Figure 2 and 3 with Figure 1 and 4, that organic compound C, cycro-ether, does not affect the gate oxide reliability.

3-3 Thermal stability of organic compounds

In order to evaluated the thermal stability of organic compounds, DOP was selected as organic contaminants, because it is a kind of benzenoid including carbon - oxygen (C-O and C=O) bonds. Figure 5 shows the results of the FTIR-ATR measurements. C-O, C=O and C-H bonds were detected from silicon substrate after contamination with DOP. FTIR-ATR is not sensitive for the detection of carbon - carbon (C=C) double bond even using Ge prism. After heat treatment, the amount of C-O, C=O and C-H bonds on the silicon substrate surface decreased. On the contrary, the number of carbon-carbon (C-C) single bonds increased with increasing heat treatment temperature. It is suggested that organic compounds, decomposed on the silicon substrate surface, are not completely vaporized from the surface and partially recomposed in the form of amorphous carbon on the surface. These results are confirmed by XPS analysis as shown in Figure 6. The XPS spectra show that the number of C-O and C=O bonds decreases and the number of C-C (C-H bond is not separated in XPS) bond increases with the heat treatment temperature. Though the signal from benzenoid is weak for all samples and the amount is not evaluated, C-C bonds are assumed to be originated from the breaking of C=C bonds.

According to FTIR-ATR and XPS spectra, organic compounds cannot be completely removed by heat treatment. These compounds are decomposed and partially recomposed into amorphous carbon on the silicon substrate surface. The gate oxide reliability was degraded by organic compounds A and B, which are benzenoid. It is suggested that comparatively heavy organic compounds behave like DOP, which is benzenoid, on the silicon substrate surface during heat treatment. Organic compounds A and B, which contain the C=C structure, cannot be completely removed by wet ashing only, neither by a following heat treatment.

4. Conclusion

Organic compounds, which are benzenoid, were found to be the cause of the reliability deterioration of gate oxide films, because these organic compounds remaining on the silicon substrate surface before oxidation can hardly be removed by heat treatment only.

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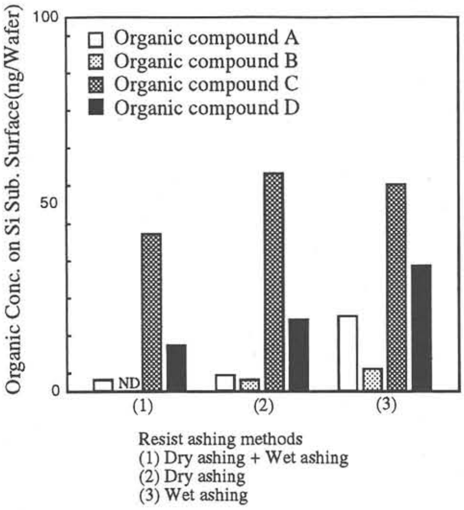


Fig. 1 Organic concentration on the silicon substrate surface for 3 resist ashing methods.

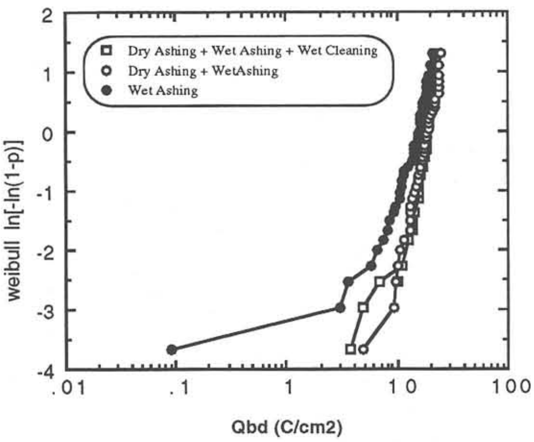
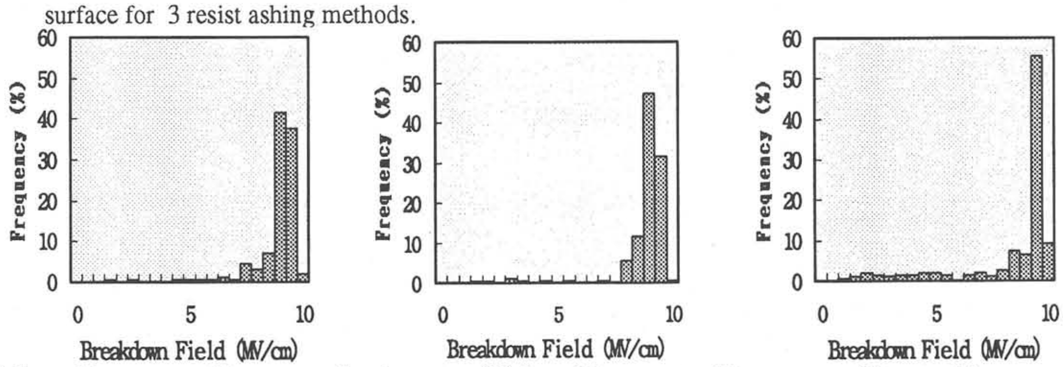


Fig. 2 Dependence of TDDB characteristics on the resist ashing method.



(1) dry ashing + wet ashing + wet cleaning. (2) dry ashing + wet ashing. (3) wet ashing.

Fig. 3 Breakdown voltage of gate oxide films after several ashing methods.

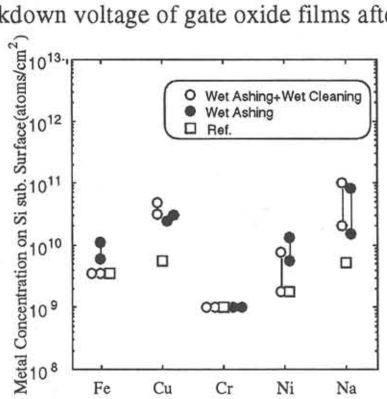


Fig. 4 Metal concentration on silicon substrate surface vs. resist ashing methods.

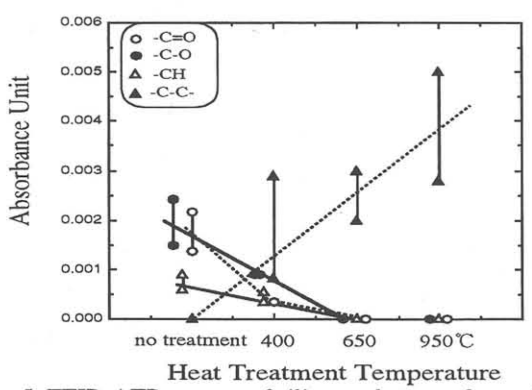


Fig. 5 FTIR-ATR spectra of silicon substrates for various heat treatment temperatures.

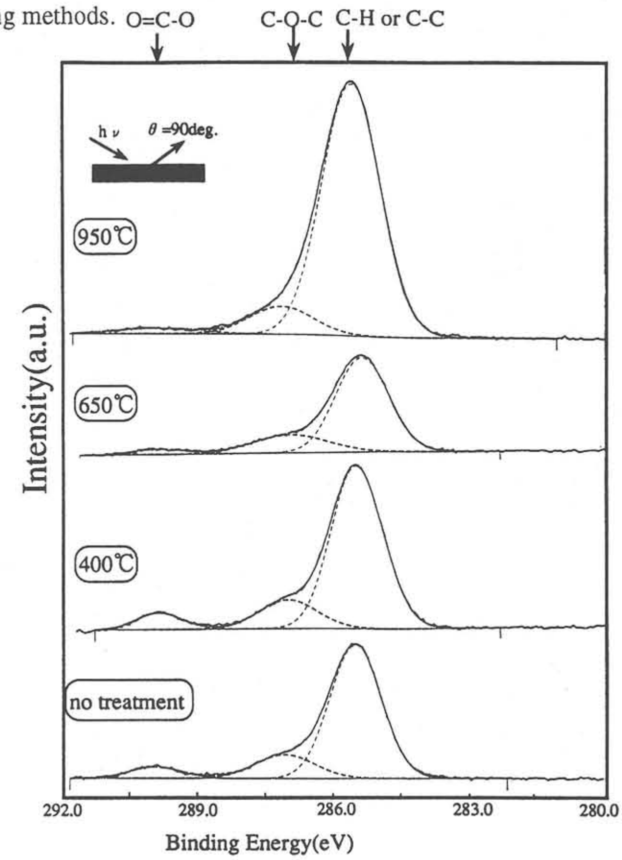


Fig.6 XPS spectra of silicon substrates for various heat temperatures.