Surface contamination control during plasma etching

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ABSTRACT

Reactive ion etching (RIE) is developed by employing NF_3 gas in order to avoid the fluorocarbon contamination on the Si surface exposed to the plasma. A high SiO₂ etch rate is achieved with magnetically enhanced RIE because of efficient species generation. An anisotropic etching profile of SiO₂ is obtained due to the low pressure and low temperature operation. The reaction layers on Si surfaces are investigated by x-ray photoelectron spectroscopy and cross-sectional transmission electron microscopy. It is found that the NF₃ plasma etching is more effective to maintain a clean surface than the CHF₃ plasma etching. In addition the photoresist which is used as a mask during via-hole etching is easily removed without any residues by O₂ plasma ashing because the fluorocarbon contamination is avoided.

1. INTRODUCTION

Contamination control of a Si surface during plasma etching is required for fabrication of a high quality device. Fluorocarbon plasmas have been studied extensively and have been used for etching polysilicon and silicon oxide. However, device degradation is caused by contamination originating from fluorocarbon deposition during dry etching.¹ The polymer deposition on the silicon surface in an NF₃ discharge is minimal compared to etching in a fluorocarbon plasma. The NF₃ gas plasma is often used for surface cleaning treatment after conventional reactive ion etching (RIE) to remove the fluorocarbon film deposited from the reactive gas plasma.²⁻⁴

In this work, an RIE process was developed by employing NF_3 gas. A high SiO₂ etch rate was achieved and an anisotropic etching profile was formed in the NF_3 plasma with magnetically enhanced RIE (MERIE). The composition of reaction layers on Si surfaces exposed to the plasma was investigated by x-ray photoelectron spectroscopy (XPS). The surface quality of the Si substrate was also characterized by cross-sectional transmission electron microscopy (TEM) in more detail.

2. EXPERIMENTAL

The MERIE system was used in this study. The wafers were clamped to the rf powered electrode. Helium back side cooling was used to main-

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tain a constant wafer temperature. Clean (100) Si wafers were etched with 700 W of rf power applied using NF_3 or CHF_3 for 60 sec. The chamber pressure was 50 mTorr and the electrode temperature was 5°C. The other process parameters such as gas flow (40 sccm) and magnetic field strength (90 G) were held constant in this experiment.

The surface of the wafers was analyzed using XPS. The XPS spectra were excited with Mg K α x-ray at 10 kV. For TEM observation (011) cross-sectional specimens were prepared. The observation of surface profile imaging was carried out with a high-resolution electron microscope operated at 200 kV.

SiO₂ etch rates were measured on samples that consisted of thermally grown SiO₂ layer on a silicon substrate with a photoresist mask. The SiO₂ profiles etched by NF₃ gas were observed using scanning electron microscopy (SEM). The chamber pressure was varied from 20 to 200 mTorr and the electrode temperature was varied from -50 to 20 $^{\circ}C$. Finally, the surface residues of the samples after via-hole etching at low pressure (20 mTorr) and low temperature (-50 °C) were investigated by SEM. The samples were observed after the resist removal by O_2 plasma ashing.

3. RESULTS AND DISCUSSION

XPS spectra of the Si sample etched by NF_3 and CHF_3 gas are shown in Fig.1. The intensities of the Si 2s and 2p peaks are strong for the sample etched in NF_3 . For the sample etched in CHF_3 they are weak. For the NF₃ etched sample peaks due to O Auger, O 1s, F Auger and F 1s are observed, and the C 1s peak is very small. For the CHF3 etched sample the peaks due to oxygen appear to be smaller, while the peaks due to fluorine and the C 1s peak is much larger. This results can be simply explained by the formation of a fluorocarbon layer on the Si surface after etching in CHF_3 . On the other hand there is an oxide layer which contains F atoms on the surface exposed in NF3.

In Fig.2 cross-sectional TEM images of NF3 and CHF3 plasma-exposed Si surface are shown. It shows (200) lattice planes parallel to the Si surface. The (200) plane spacing is 0.27 nm. For the NF_3 etched sample there are no defects in evidence and the Si surface is smooth within a few monolayers [Fig.2(a)]. Extensive defects are found in the surface layer after etching in CHF_3 [Fig.2 (b)]. Small amorphouslike regions and a high density of planer defects are observed. They are heavily decorated by impurities, possibly H, C or F.⁵ Figure 2(a) shows the presence of a 2 nm thick amorphous film (indicated by arrows) which was found by XPS to contain mostly oxygen and thus represents the native oxide on the surface exposed in NF_3 . As shown in Fig.2(b) a 3 nm thick amorphous film (also indicated by arrows) on the surface etched by $ext{CHF}_3$ is observed. This film was identified to be a fluorocarbon film by XPS.

Figure 3 shows the etch rates of SiO_2 in NF_3 as a function of pressure. It is noted that the SiO2 etch rate does not change very much with pressure. A high SiO2 etch rate is achieved with the MERIE because of efficient species generation. Figure 4 shows the etch rates of SiO2 as a function of temperature. The SiO2 etch rate slightly

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increases with lowering temperature but it keeps nearly constant within the temperature range from -50 to 20 °C.

SEM micrographs of the samples after the resist removal by O2 ashing are shown in Fig.5. For the sample etched at the NF3 pressure of 200 mTorr and the temperature of 5 °C, the sidewall profile is slightly bowed with a positive taper [Fig.5(a)]. As the pressure is decreased to 20 mTorr, the bowed feature of the sidewall disappears and the profile exhibits a slightly positive slope [Fig.5(b)]. For the sample etched at the temperature of -50 °C and the NF₃ pressure of 20 mTorr, the straight sidewall is produced [Fig.5(c)]. An anisotropic etching profile is formed due to low pressure and low temperature operation. Etching at higher pressures tends towards chemical processes where ion energies are lower and the density of reactive species is higher. Etching at lower pressures emphasizes physical processes and etching at lower temperatures further enhances them. Figure 5(d) shows the cross-sectional view of the sample etched in CHF₃ at the temperature of -50 °C and the pressure of 20 mTorr. The tapered sidewall is formed. The tapered etching profile is attained by the simultaneous progress of etching and deposition. The deposition of a fluorocarbon film on the sidewall induces the tapered profile formation at the low temperature.⁶ During SiO₂ etching in NF₃ the polymer film is not deposited on the sidewall for lack of deposition gas such as hydrocarbon. For the sample etched in NF_3 on the same etching condition as CHF₃, therefore, the straight sidewall is obtained.

Figure 6 shows the profile of the via-hole etched in NF₃ at the temperature of -50 °C and the pressure of 20 mTorr. The samples were treated in HF solution before the plasma etching in NF₃. Undercutting by the HF treatment is observed at the interface between the photoresist and the SiO₂ film. The surface residues of the samples etched in NF₃ and CHF₃ after the resist removal by O₂ ashing are shown in Fig.7. For the sample etched in CHF₃ the residual films still remain around the via-holes [Fig.7(b)]. The fluorocarbon film which contains Al atoms sputtered during overetching was redeposited on the sidewall and the surface of the photoresist. On the sample etched in NF₃ there are no residues [Fig.7(a)], because the fluorocarbon contamination is avoided.

4. CONCLUSION

The surface modification in Si substrate induced during plasma etching was studied by XPS and cross-sectional TEM. For pure NF₃ etching gas, a native oxide film 2 nm thick grown on the Si surface was observed and there were no extended surface defects. It was found that the NF₃ plasma etching was effective to maintain a clean surface as compared to the sample exposed to the CHF₃ plasma. In addition, the photoresist used during via-hole etching was easily removed without any residues by O_2 ashing because the fluorocarbon contamination was avoided. A clean RIE process was developed by employing the NF₃ gas. A high SiO₂ etch rate was achieved and an anisotropic etching profile was obtained in the NF₃ plasma with the MERIE.

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Fig.1. XPS spectra of NF_3 and CHF_3 etched Si samples.

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Fig.2. TEM cross sections of Si surface etched in (a) $\rm NF_3$ and (b) $\rm CHF_3$ plasmas.

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