Surface contamination control during plasma etching

H. Miyatake, K. Kawai, N. Fujiwara, M. Yoneda, K. Nishioka" and H. Abe

LSI Laboratory, Mitsubishi Electric Corporation, 4-1 Mizuhara, Itami, Hyogo 664, Japan +Kita-Itami Works, Mitsubishi Electric Corporation, 4-1 Mizuhara, Itami, Hyogo 664, Japan

### 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 SiO<sub>2</sub> etch rate is achieved with magnetically enhanced RIE because of efficient species generation. An anisotropic etching profile of SiO<sub>2</sub> 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 NFg plasma etching is more effective to maintain a clean surface than the CHF<sub>3</sub> plasma etching. In addition the photoresist which is used as <sup>a</sup> mask during via-hole etching is easily removed without any residues by  $O_2$ plasma ashing because the fluorocarbon contamination is avoided.

### 1. INTRODUCTION

Contamination control of <sup>a</sup> Si surface during plasma etching is required for fabrication of <sup>a</sup> 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. The polymer deposition on the silicon surface in an  $NF_3$ discharge is minimal compared to etching in <sup>a</sup> fluorocarbon plasma. The  $NF<sub>3</sub>$  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.  $2<sup>-2</sup>$ 

In this work, an RIE process was developed by employing NF<sub>3</sub> gas. A high SiQg etch rate was achieved and an anisotropic etching profile was formed in the NF<sub>3</sub> 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 crosssectional 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-

DOCKET

**IP Bridge Exhibit 2223**  IP Bridge Exhibit 2223 IP Bridge Exhibit 2223<br>TSMC v. Godo Kaisha IP Bridge 1 **IRRA017** 010*1*3

 $L \, A \, R \, M$  Find authenticated [court documents without watermarks](https://www.docketalarm.com/) at **docketalarm.com**.

tain <sup>a</sup> 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 <sup>50</sup> mTorr and the electrode temperature was 5°C. The other process parameters such as gas flow (40 scem) 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 Kg x-ray at <sup>10</sup> kV. For TEM observation (011) cross-sectional specimens were prepared. The observation of surface profile imaging was carried out with <sup>a</sup> high-resolution electron microscope operated at 200 kV.

 $SiO<sub>2</sub>$  etch rates were measured on samples that consisted of thermally grown SiO<sub>2</sub> layer on a silicon substrate with a photoresist mask. The  $SiO_2$  profiles etched by NF<sub>3</sub> gas were observed using scanning electron microscopy (SEM). The chamber pressure was varied from <sup>20</sup> to 200 mTorr and the electrode temperature was varied from -50 to 20 °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<sub>2</sub> plasma ashing.

### 3.RESULTS AND DISCUSSION

XPS spectra of the Si sample etched by  $NF<sub>3</sub>$  and  $CHF<sub>3</sub>$  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 NF<sub>3</sub> etched sample peaks due to O Auger, O 1s,  $\breve{F}$  Auger and F 1s are observed, and the C 1s peak is very small. For the CHF<sub>3</sub> etched sample the peaks due to oxygen appear to be smaller, while the peaks due to fluorine and the <sup>C</sup> ls peak is much larger. This results can be simply explained by the formation of <sup>a</sup> 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  $NF_3$ .

In Fig. 2 cross-sectional TEM images of  $NF<sub>3</sub>$  and  $CHF<sub>3</sub>$  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<sub>3</sub> etched sample there are no defects in evidence and the Si surface is smooth within <sup>a</sup> few monolayers [Fig.2(a)]. Extensive defects are found in the surface layer after etching in CHF<sub>3</sub> [Fig.2 (b)]. Small amorphouslike regions and <sup>a</sup> high density of planer defects are observed. They are heavily decorated by impurities, possibly H, C or  $F \cdot 5$  Figure 2(a) shows the presence of <sup>a</sup> <sup>2</sup> 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 CHF<sub>3</sub> is observed. This film was identified to be a fluorocarbon film by XPS.

Figure 3 shows the etch rates of  $SiO_2$  in NF<sub>3</sub> as a function of pressure. It is noted that the SiO<sub>2</sub> etch rate does not change very much with pressure. A high  $SiO_2$  etch rate is achieved with the MERIE because of efficient species generation. Figure <sup>4</sup> shows the etch rates of SiO<sub>2</sub> as a function of temperature. The SiO<sub>2</sub> etch rate slightly

**DOCKET** 

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  $O_2$ ashing are shown in Fig.5. For the sample etched at the NF<sub>3</sub> pressure of 200 mTorr and the temperature of 5 °C, the sidewall profile is slightly bowed with <sup>a</sup> positive taper [Fig.5{a)]. As the pressure is decreased to 20 mTorr, the bowed feature of the sidewall disappears and the profile exhibits <sup>a</sup> slightly positive slope [Fig.5(b)]. For the sample etched at the temperature of  $-50^{\circ}$ C and the NF<sub>3</sub> pressure of 20 sample elemed at the temperature of 5000 and the M<sub>3</sub> pressure of 20<br>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  $CHF<sub>3</sub>$  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 <sup>a</sup> fluorocarbon film on the sidewall induces the tapered profile formation at the low temperature.  $^6$  During SiO<sub>2</sub> etching in NF<sub>3</sub> the polymer film is not deposited on the sidewall for lack of deposition gas such as hydrocarbon. For the sample etched in  $NF<sub>3</sub>$  on the same etching condition as  $CHF_3$ , therefore, the straight sidewall is obtained.

Figure 6 shows the profile of the via-hole etched in  $NF<sub>3</sub>$  at the temperature of -50°C and the pressure of 20 mTorr. The samples were treated in HF solution before the plasma etching in  $NF_3$ . Undercutting by the HF treatment is observed at the interface between the photoresist and the SiO<sub>2</sub> film. The surface residues of the samples etched in  $NF<sub>3</sub>$  and CHF<sub>3</sub> after the resist removal by  $O<sub>2</sub>$  ashing are shown in Fig.7. For the sample etched in CHF<sub>3</sub> 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 NF<sub>3</sub> 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 NF<sub>3</sub> etching gas, <sup>a</sup> native oxide film <sup>2</sup> nm thick grown on the Si surface was observed and there were no extended surface defects. It was found that the  $NF_{3}$  plasma etching was effective to maintain a clean surface as compared to the sample exposed to the CHF<sub>3</sub> 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  $\bar{\text{RIE}}$  process was developed by employing the  $\text{NF}_3$  gas. A high SiO<sub>2</sub> etch rate was achieved and an anisotropic etching profile was obtained in the  $NF_3$  plasma with the MERIE.

**DOCKET** 

### 5. REFERENCES

1. Y. H. Lee, G. S. Oehriein and C. Ranson, "RIE-Induced Damage and Contamination in Silicon," Radiation Effects and Defects in Solids, vol.111&112, pp.221-232, 1989.

2. H. Cerva, E. G. Mohr and H. Oppolzer, "Transmission Electron Microscope Study of Lattice Damage and Polymer Coating Formed after Reactive Ion Etching of  $\text{SiO}_2$ ," J. Vac. Sci. Technol., vol.B5, no.2, pp-590-593, 1987.

3. T. Akimoto, K. Kasama and M. Sakamoto, "Removal of RIE Induced Damage Layer Using  $NF_3/O_2$  Chemical Dry Etching," Proc. of 10th Symposium on Dry Process, pp.92-97, 1988.

4. T. Ogawa, K. Kawai, H. Ito, M. Yoneda and K. Nishioka, "Si Surface Cleaning Using NF<sub>3</sub> after Glow Plasma and Deep UV Irradiation," Proc. of llth Symposium on Dry Process, pp.94-99, 1989.

5. S. J. Jeng and G. S. Oehrlein, "Microstructural Studies of Reactive lon Etched Silicon,' Appl. Phys. Lett., vol.50, no.26, pp.1912- 1914, 1987.

6. T. Ohiwa, K. Horioka, T. Arikado, I. Hasegawa and H. Okano, "SiOg Tapered etching employing Magnetron Discharge," Proc. of 12th Symposium on Dry Process, pp.105-109, 1990.



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

 $\mathcal{S} \cap \mathcal{K}$  for  $\mathcal{S}$ 



Fig.2. TEM cross sections of Si surface etched in (a)  $NF<sub>3</sub>$  and (b)  $CHF<sub>3</sub>$ plasmas.

### DOCKE<sup>-</sup> R Find authenticated [court documents without watermarks](https://www.docketalarm.com/) at **docketalarm.com**. M

A

# **DOCKET**



## Explore Litigation Insights

Docket Alarm provides insights to develop a more informed litigation strategy and the peace of mind of knowing you're on top of things.

## **Real-Time Litigation Alerts**



Keep your litigation team up-to-date with **real-time alerts** and advanced team management tools built for the enterprise, all while greatly reducing PACER spend.

Our comprehensive service means we can handle Federal, State, and Administrative courts across the country.

## **Advanced Docket Research**



With over 230 million records, Docket Alarm's cloud-native docket research platform finds what other services can't. Coverage includes Federal, State, plus PTAB, TTAB, ITC and NLRB decisions, all in one place.

Identify arguments that have been successful in the past with full text, pinpoint searching. Link to case law cited within any court document via Fastcase.

## **Analytics At Your Fingertips**



Learn what happened the last time a particular judge, opposing counsel or company faced cases similar to yours.

Advanced out-of-the-box PTAB and TTAB analytics are always at your fingertips.

### **API**

Docket Alarm offers a powerful API (application programming interface) to developers that want to integrate case filings into their apps.

### **LAW FIRMS**

Build custom dashboards for your attorneys and clients with live data direct from the court.

Automate many repetitive legal tasks like conflict checks, document management, and marketing.

### **FINANCIAL INSTITUTIONS**

Litigation and bankruptcy checks for companies and debtors.

### **E-DISCOVERY AND LEGAL VENDORS**

Sync your system to PACER to automate legal marketing.

