IN SITU FOURIER TRANSFORM INFRARED ELLIPSOMETRY FOR MONITORING c-Si ETCHING PROCESS BY CF_4 PLASMA

T. Shirafuji, K. Tachibana† and S. Muraishi††

Department of Electronics and Information Science,
Kyoto Institute of Technology, Matsugasaki, Sakyo-Ku, Kyoto 606, Japan
†Department of Electrical and Electronic Engineering, Kyoto Univerisity,
Yoshida Hommmachi, Sakyo-Ku, Kyoto 606, Japan
††Application and Research Center, JEOL
1-2 Musashino 3 Chome, Akishima, Tokyo 196, Japan

Abstract

A Fourier-transform infrared phase-modulated spectroscopic ellipsometry has been applied to *in situ* monitoring of c-Si surface treated by a parallel-plate RF plasma of CF_4 gas. Formation of fluorocarbon layer on the grounded electrode and fluorosilicon layer on the powered electrode have been identified from measured spectra.

1. Introduction

Eching of c-Si wafers in the plasma of F-containing gases has been studied with great deal of experimental and theoretical efforts, and basic mechanisms have been clarified on the basis of the results in the simplified conditions using XeF_2[1] and F_2[2]. Realistic RIE, however, mostly utilizes plasma of fluorocarbon gases[3]. Gas-phase and surface physics and chemistry become more complicated in this system due to the formation of fluorocarbon layer and surface roughness. Current activities for understanding the RIE are mostly aimed at gas-phase chemistry[4], and few attempts are made at surface where the etching proceeds actually. In this paper, we report on the results of *in situ* monitoring of c-Si surface in CF_4 plasma by using a FT-IR phase modulated spectroscopic ellipsometer (PMSE)[5].

2. Experimental

Figure 1 shows the schematic diagram of our FT-IR PMSE combined with a capacitively coupled RF plasma reactor for *in situ* surface investigation. The configuration consists of a conventional FT-IR spectrometer as a light source (JEOL JIR-7000), a poralizer, a photoelastic modulator (PEM) (Hinds PEM-90), a sample (c-Si wafer), folding mirrors M_1-M_2, an analyzer and a mercury-cadmium-telluride (MCT)

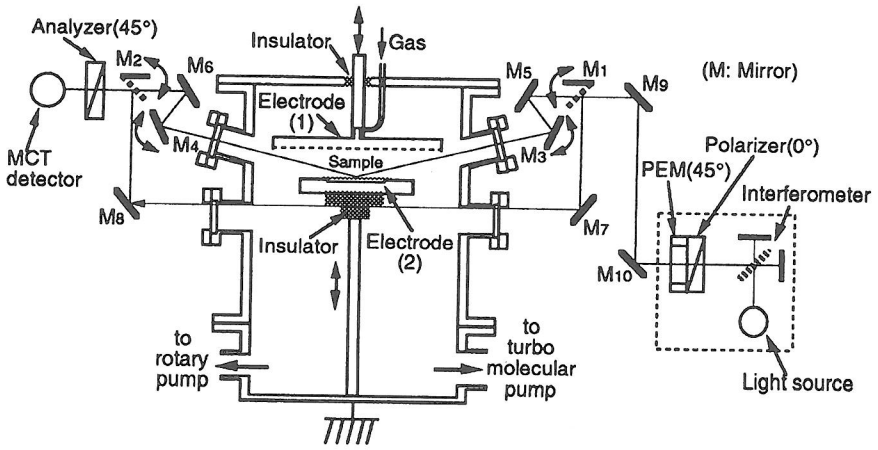

Fig.1 Experimental setup for an FT-IR PME system equipped to a conventional capacitively coupled RF plasma reactor.

detector cooled with liquid nitrogen. Modulation frequency (f) of the PEM is 37kHz. The azimuth angle of the poralizer, modulator and analyzer are 0°, 45° and 45°, respectively. Windows for the IR beam are made of KBr. The incidence angle of the IR beam on the wafer is 75°.

Spectral resolution was $4cm^{-1}$. Spectra of ellipsometric parameters Ψ and Δ were calculated after 500-scans accumulation of dc, f and $2f$ signals detected through low-pass filer and lock-in amplifier. The accumulation took approximately 30 minutes. Optical density D was calculated with the following equation[5],

$$D = \mathrm{Re}\{D\} + i\,\mathrm{Im}\{D\} = \ln[\tan\Psi_{sub} / \tan\Psi] + i\,(\Delta_{sub} - \Delta)$$

In this equation, the subscript 'sub' means the value for the substrate before plasma treatment. $\mathrm{Re}\{D\}$ and $\mathrm{Im}\{D\}$ are proportional to imaginary and real part of dielectric function of surface over layer, and also to its thickness. Therefore, $\mathrm{Re}\{D\}$ and $\mathrm{Im}\{D\}$ have a Kramers-Kronig relationship, that is, a $\mathrm{Re}\{D\}$ peak appears as a gaussian peak and a $\mathrm{Im}\{D\}$ peak does as its differential.

In our setup, transmission absorption spectroscopy can also be performed by changing the angle of the two mirrors, M_1 and M_2. The IR beam for absorption spectroscopy passes just above the wafer surface, and the distance between the beam and the surface is approximately 5mm. Pass length in the chamber is approximately 30cm. Absorbance spectrum has been calculated by subtracting the spectrum taken under evacuated condition. For the purpose of relative comparision, the spectrum has been normalized with the absorbance value of CF_4 peak at $1283cm^{-1}$ for pure CF_4 gas without discharge. The peaks have been assigned according to ref.6.

CF_4 plasma treatment was carried out on c-Si(100) wafer ($5x5cm^2$). Temperature of the wafer was not controlled intentionally. The back surface of the wafer was

roughened, and it was separated from the holder surface by 5mm in order to reduce the interference in the spectrum caused by multiple reflection. The diameter of RF electrode was 16cm. Flow rate, pressure and RF power were 8sccm, 0.2Torr and 100W, respectively. The PMSE measurement was carried out under evacuated condition after each CF_4 plasma treatment.

3. Results and Discussion

3.1 Gas-phase diagnostics

Figure 2 shows IR transmission absorbance spectra for CF_4 plasma taken above a c-Si wafer on the grounded (GND) and powered (RF) electrodes and for CF_4 gas without discharge. In the present experimental condition, dissociation degree of CF_4 is found to be 20-30% by comparing the height of CF_4 peak at 1283cm^{-1}. As the species generated through the dissociation of CF_4, CF_3 and CF_2 are detected at 1250cm^{-1} and 1115cm^{-1}, respectively. CF peak at 1279cm^{-1} cannot be distinguished from CF_4 peak. In addition to these fluorocarbon peaks, SiF_4 peak appears at 1028cm^{-1} due to eching of c-Si wafer. The peak height taken above the RF electrode is slightly higher than that above the GND electrode. Altough diffusional transport occurs in gas phase, this shows higher etching rate on the RF electrode. Although SiF_2 is known to be an alternative eching product, it is not identified in the corresponding band around 850cm^{-1}.

Density of these species are summarized in **Table I**. The density of CF_2 and CF_3 has been calculated from integrated absorption coefficient for these peaks[7]. The density of SiF_4 has been calculated from peak absorption coefficient with a

Table I. Estimated density of CF_4, CF_3, CF_2 and SiF_4 (in cm^{-3}).

RF	CF_4	CF_3	CF_2	SiF_4	Sum
0W	6.44×10^{15}	0	0	0	6.44×10^{15}
100W	4.71×10^{15}	5.40×10^{14}	7.50×10^{14}	2.79×10^{14}	6.28×10^{15}

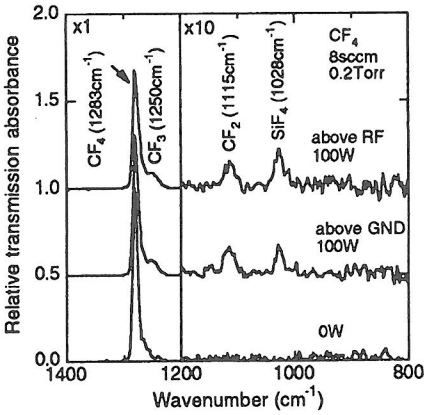

Fig.2 IR transmission spectra of CF_4 plasmas.

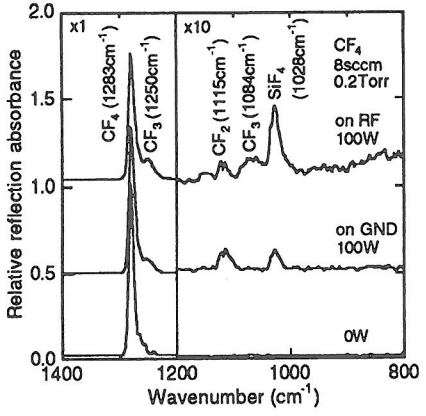

Fig.3 IR reflectance spectra of CF_4 plasmas.

proportionality constant of $3.53 \times 10^{-18} cm^2$, which has been determined by measuring absorption coefficient for pure SiF_4 gas under known pressure. As can be seen in the table, density of CF_2, CF_3 and SiF_4 is about 10% of CF_4. In order to estimate the upper limit of SiF_2 density, we have tried a measurement in SiF_4 plasma. However, SiF_2 peak cannot be detected under the condition of 0.2Torr and100W. A simulation of gas phase reactions in SiF_4 plasma using a one dimensional fluid model predicts SiF_2 density is in the order of $10^{10} cm^{-3}$. Therefore, the density of SiF_2 in CF_4 plasma is regarded to be less than 10^9-$10^{10} cm^{-3}$. From these results, we can conclude that major etching product in the gas phase is SiF_4 in CF_4 plasma.

Figure 3 shows IR reflection absorbance spectra of c-Si wafer in CF_4 plasma. As we have not subtract the gas-phase absorption, the spectra contain both gas phase and surface contribution. If the surface (or near surface) absorption is negligible, the spectra in **Fig.3** must be similar to those in **Fig.2** obtained in the gas phase. Comparing these figures, we can see that the spectrum reflected on the RF electrode shows remarkably differs from that on the GND electrode. In te former, CF_3 peak at $1250 cm^{-1}$ shows higher intensity than in the gas phase spectrum, and another clear peak assigned to CF_3 appears at $1084 cm^{-1}$, which cannot be identified in **Fig.2**. In addition, SiF_4 peak shows much higher intensity. These difference show that RAS spectra contain the surface absorption,

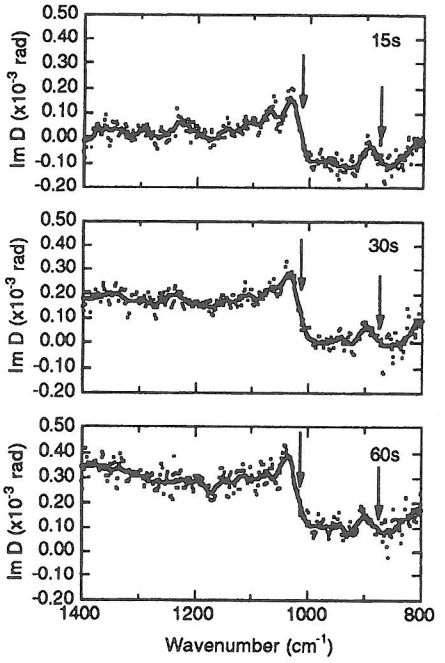

Fig.4 Temporal behavior of Im{D} spectra for c-Si surface treated with CF_4 plasma on RF electrode.

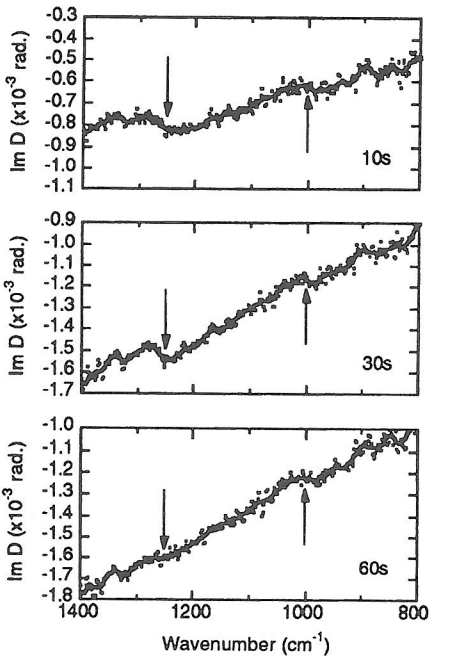

Fig.5 Temporal behavior of Im{D} spectra for c-Si surface treated with CF_4 plasma on GND electrode.

and the difference between the RF side and the GND side is attributed to the difference in the self bias. Higher intensity of SiF_4 peak on the RF side is due to higher rate of c-Si eching, and the production of SiF_4 become larger. Higher intensity of CF_3 peak may be due to its production in the etching of polymerized CF_2 on the surface.

3.2 Surface diagnostics

Figure 4 shows spectra of Im{D} for c-Si surface treated with CF_4 plasma on the RF electrode for 15, 30 and 60 seconds. Etching rate was 3-5Å/s, which was determined in the etching of poly-silicon film formed on quartz substrate by spectroscopic ellipsometry in visible region. In the figure, two differential peaks appear at approximately 1010 and 870cm^{-1}, which are assingend to SiF_4 and SiF_2, respectively. As the major gas phase species is SiF_4, SiF_2 formed on the surface does not desorb as it is, and it must turn into SiF_4 on the surface. Appearance of the SiF_4 peak suggests that SiF_4 molecules produced through the etching process still remain on the substrate surface although this species is volatile. The peak intensity and the absolute value of Im{D} does not change so much with increasing the treatment time. This means that the thickness of the overlayer (presumably fluorinated layer) does not change during etching. This tendency is similar to the result obtained in spontaneous etching with XeF_2[1], although the existence of SiF_4 is not identified.

Figure 5 shows Im{D} spectra for c-Si surface treated on the GND electrode. SiF_4 peak appears at 1010cm^{-1}, and SiF_2 peak also appears around 870cm^{-1} although it is not so clear as in the case of RF electrode. In addition, a peak at 1250cm^{-1} appears, and it is assigned to CF_3. In this case, the base line of Im{D} spectra changes more rapidly than that in Fig.4. This means that relatively thick fluorocarbon film is formed on the surface.

In order to verify the peak assingment, we have measured the c-Si surface exposed to F_2. **Figure 6** shows Im{D} spectra of the surface exposed to 5%F_2 diluted with He at 0.5Torr for 5min. As seen in the figure, a peak is found at 850cm^{-1}, which corresponding to SiF_2. This means F_2 molecules adsorb dissociatively on the surface to forms SiF_2 bonds. **Figure 7**

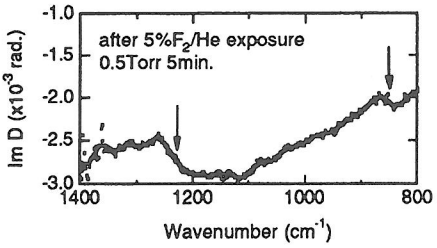

Fig.6 Im{D} spectrum for c-Si surface exposed to 5%F_2/He for 5 minutes.

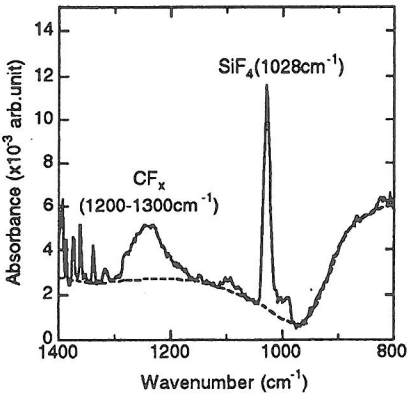

Fig.7 Transmission absorbance of gas phase during F_2-exposure experiment.

shows transmission absorption spectrum in gas phase during F_2 exposure, in which a SiF_4 peak clearly appears at 1028cm^{-1}. Therefore, F_2 molecules form SiF_2 bonds on the surface, and the SiF_2 bonds desorb out as SiF_4 molecules. However, SiF_4 is not found in the surface spectrum, while it is found for CF_4 plasma treatment. Therefore, remaining SiF_4 on the surface treated with CF_4 plasma is regarded to be piled in fluorinated layer. Although a broad peak around1250cm^{-1} corresponding to fluorocarbon is found in Fig.7 even though no fluorocarbon gas is used, this is considered to be due to removal of fluorocarbon film from chamber wall and re-deposition on the surface.

5. Conclusion

In conclusion, an FT-IR PMSE has been applied to monitoring of c-Si surface treated with CF_4 plasma. Gas-phase transmission absorption spectroscopy and simple reflection spectroscopy have also been carried out.

Gas-phase abosorption spectroscopy has revealed that major etching product in gas phase is SiF_4, and the density of SiF_2 is much lower.

PMSE measurement has shown that SiF_4 and SiF_2 exist on the surface after the treatment on the RF electrode, while CF_x also exist on the GND electrode. An F_2 exposure experiment has shown that SiF_4 is dominant in gas phase and only SiF_2 exists on the surface, which suggests that SiF_2 turns into SiF_4 to desorb out. Pile up of SiF_4 in the case of CF_4 treatment is considered to be peculiar to this treatment.

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