FOURIER TRANSFORM INFRARED DIAGNOSTICS OF REACTION PRODUCTS DURING ELECTRON CYCLOTRON RESONANCE PLASMA ETCHING OF Si IN Cl_2

Kouichi Ono, Kazuyasu Nishikawa, Mutumi Tuda, and Tatsuo Oomori

Semiconductor Research Laboratory, Mitsubishi Electric Corporation,
Tsukaguchi-Honmachi, Amagasaki, Hyogo 661, Japan

Abstract *In situ* Fourier transform infrared (FTIR) absorption spectroscopy has been used for detection of reaction products during electron cyclotron resonance (ECR) plasma etching of Si in Cl_2. Silicon tetrachloride $SiCl_4$ was the only IR-absorbing etch product species detected in the gas phase, while unsaturated $SiCl_x$ (x=1-3) as well as $SiCl_4$ were observed on the surface by reflection absorption spectrosopy (RAS). Moreover, a broad absorption feature due to silicon oxides SiO was unexpectedly found to occur both in the gas phase and on the surface, presumably arising from background oxygen due to a small leak. Absolute calibration was made to estimate the concentrations of product species $SiCl_4$ and SiO in the discharge: at a pressure of 0.5 mTorr, e.g., $[SiCl_4]\sim 1\times10^{13}$ cm^{-3} or comparable to the feedstock Cl_2 gas densties, and $[SiO]\sim 8\times10^{11}$ cm^{-3} or more than one order of magnitude lower than $[SiCl_4]$ and $[Cl_2]$.

1. Introduction

It is generally appreciated that in plasma etching, the incoming ions and neutrals onto the substrate primarily govern the etching characteristics such as etch rates, profiles, and selectivities [1,2]. On the other hand, it has recently been assumed that product species, desorbed from the substrate as a result of etching reactions, also play an important role in processing [3]; in effect, the redissociation of reaction products results in the redeposition and resupply of reactant species onto the surface, and the readsorption of products themselves may also be taken into account. Such effects of reaction products become more significant for etching processes in low-pressure, high-density plasma sources, such as electron cyclotron resonance (ECR), where partial pressures of product species are expected to be high during processing owing to high etch rates achieved at low feedstock gas densities. Thus, diagnostic studies are required to characterize reaction products as well as reactants, to further understand what limits the etch rates, profiles, selectivities, etc. in these plasma etching environments.

This paper presents *in situ* Fourier transform infrared (FTIR) diagnostics of etch poduct species during ECR plasma etching of Si in Cl_2. The *in situ* observation was made in the gas phase above the substrate by transmission absorption spectroscopy, and also on the substrate surface by reflection absorption spectroscopy (RAS). In plasma processing, optical emission spectroscopy (OES) and laser-induced fluorescence (LIF) in the uv and visible are widely used *in situ* plasma diagnostic techniques for detection of reactive species in the discharge [4]; however, it is difficult to identify molecular product species with more than two or three atoms with these techniques which are sensitive particularly to atoms, ions, and smaller radicals. On the other hand, infrared absorption spectroscopy such as FTIR is better suited for detection of triatomic and larger molecules not easily probed by OES and LIF, and thus the FTIR complements OES and LIF techniques. Moreover, FTIR has an advantage in that the information on surface chemistry can be obtained by IR-RAS. As for *in situ* FTIR diagnostics of plasma etching processes, a limited number of studies have been concerned with gas-phase product species in rf chlorine [5] and halocarbon [6] plasma etching of Si, and also with fragments as well as feedstock gas densities in rf [7] and ECR [8] fluorocarbon plasmas.

2. Experiment

Figure 1 shows the experimental setup similar to that described previously [9,10]. Briefly, the ECR plasma reactor consisted of a plasma chamber and a specimen chamber. A set of solenoid coils were placed around the former, providing a divergent magnetic field to produce and transport ECR plasmas to a sample for etching in the specimen chamber. The discharge was established by 2.45-GHz right-hand circularly polarized microwaves of TE_{11} mode, and the 875-G ECR resonance was located near the end of the plasma chamber. Pure Cl_2 gas was introduced into the reactor, evacuated to a base pressure $<10^{-6}$ Torr, through a set of small holes around the microwave entrance window. The specimen chamber, 40 cm in diameter and 40 cm long, had an end port for pumping and side ports for diagnostics, containing a 16-cm-diam floating electrode or substrate holder at ~32 cm downstream ($B \approx 160$ G) from the ECR resonance region. The electrode was water cooled, and capacitively coupled to a 13.56-MHz rf power supply through an impedance matching network for additional rf biasing. Most of the experiments were performed at an incident microwave power of 600 W and a gas flow rate of 7 sccm; the reactor gas pressure was varied from $P_0=10$ to 0.2 mTorr (1.33 to 0.0266 Pa).

In FTIR diagnostics of etch-related chemical species, as shown in Fig. 1, the infrared optical system consisted of an FTIR spectrometer (JEOL JIR-7000) which was reconfigured for the probe beam to pass through the specimen chamber located outside of the optical bench of the instrument. In transmission absorption spectroscopy for observation of gas-phase product species [9,10], the IR beam from the FTIR bench was directed through 4-cm-diam KBr optical flats into the discharge, ~4 cm above the substrate parallel to its surface. The total absorption path length in the system was $\ell \approx 50$ cm, and changes in the IR beam intensity due to absorption by gas-phase species were detected with a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector. In RAS for

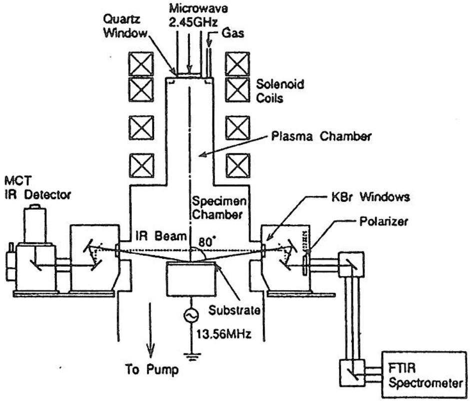

Fig. 1 Experimental setup.

observation of product species on the surface [10], the IR beam from the FTIR bench was passed through a polarizer, and the *p*-polarized beam was then focused onto the substrate surface at an incident angle of 80°. In these observations, the FTIR data were recorded at a resolution of 2 cm^{-1} by averaging over 500 scans (requiring ~8 min), and the noise level in the spectrum was not affected seriously by operating the discharge. Moreover, the transmission absorption spectra of pure SiCl$_4$ gases and plasmas were also examined for reference, because silicon chlorides SiCl$_x$ (x=1−4) are assumed to be the primary product species resulting from the etching of Si in chlorine-containing plasmas.

Samples for etching were 6-in.-diam single-crystal Si wafers for observation of reaction products in the gas phase. On the other hand, so-called buried metal layer (BML) samples [11] were used for observation of product species on the surface; they were grown on 6-in.-diam Si wafers, consisting of a 50-nm-thick layer of Ti, a 100-nm-thick buried metal layer of Au, and then 500-nm-thick films of Si. The Si thin films were sputter deposited at a temperature of ~520 K to form an overlayer of amorphous polycrystalline Si (with no detectable structure). The samples were clamped into place on the electrode, and backside helium was injected for increased wafer thermal contact.

3. Rsesults and Discussion

Figure 2(a) shows typical FTIR absorption spectra in the range 1300−500 cm^{-1} when the ECR plasma was on and off, taken in the gas phase at a Cl$_2$ pressure of P_0=0.5 mTorr; the spectra in the presence of a plasma consist of the two with and without a pre-etch breakthrough step using additional rf biasing (indicated by Si wafer active and inactive, respectively). The present etching of Si under floating substrate conditions was initiated after a pre-etch breakthrough to remove a native oxide layer on its surface, exhibiting absorption features as shown in the figure. It is further noted that these features were found to disappear after each etch run, thus the IR absorption features observed being attributable to gas-phase product species from etching, not the result of deposition on KBr windows. Moreover, the absorption spectra of pure SiCl$_4$ gases and plasmas are shown in Fig. 2(b), taken for reference with the ECR plasma on and off at a pressure of P_0=0.5 mTorr.

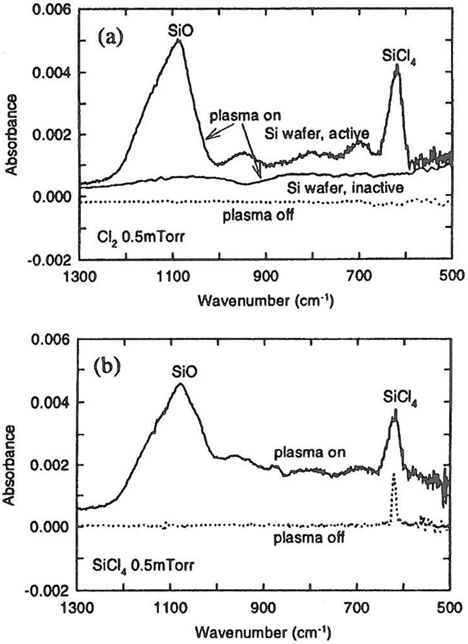

Fig. 2 FTIR absorption spectra in the gas phase with the ECR plasma on and off in (a) Cl$_2$ and (b) SiCl$_4$ at P_0=0.5 mTorr.

In these two figures, where the vertical scales of absorbance are relative to each other, the absorption spectrum during Si etching in Cl$_2$ plasmas is very similar to that of SiCl$_4$ plasmas, showing two apparent peaks around

620 and 1100 cm^{-1}; the former absorption peak is also seen in the spectrum of $SiCl_4$ gases, corresponding to the ν_3 fundamental vibrational band of $SiCl_4$ [12]. The width of the 620-cm^{-1} absorption feature of $SiCl_4$ is significantly larger in $SiCl_4$ discharge than in $SiCl_4$ gas, and the widths are similar in $SiCl_4$ discharge and in Cl_2 plasma etching of Si. Such broadening of the profile in plasmas is due to additional vibrationally excited hot bands of $SiCl_4$ around 620 cm^{-1} arising from electron-impact excitation in the discharge. The another broad absorption feature around 1100 cm^{-1} was assigned presumably to the fundamental vibrational band of SiO. In fact, this absorption feature is similar to that of the asymmetric Si-O stretching vibrational mode identified in the IR transmission spectrum of SiO_2 thin films with an absorption peak in the range 1100–1060 cm^{-1} [13].

It follows from these FTIR spectra that silicon tetrachloride $SiCl_4$ may be the only IR-absorbing etch product species detected in the gas phase during ECR plasma etching of Si in Cl_2. The absorption spectra from unsaturated silicon chlorides $SiCl_x$ (x=1–3), whose strong peaks are assumed to be in the range 600–500 cm^{-1} [14], were not observed in the discharge at the present level of detection. These results are similar to those that have already been reported for rf plasma etching of polycrystalline Si in Cl_2 at high pressures (~300 mTorr) [5]. It is further noted that silicon oxides SiO, unexpectedly found to occur in these experiments, were attributable probably to reactions between Si or silicon chlorides from etching and background oxygen due to a small leak.

Figure 3 shows FTIR absorption spectra in the gas phase during ECR plasma etching of Si in Cl_2 at different pressures P_0. The 620-cm^{-1} absorption peak of $SiCl_4$ is maximum at $P_0 \approx 0.5$ mTorr and disappears at high pressures $P_0 > 2$ mTorr. On the other hand, the absorption feature of SiO around 1100 cm^{-1} exhibits different behavior: the absorption peak is also maximum at $P_0 \approx 0.5$ mTorr, but gradually decreases with further increasing P_0; consequently, the absorption feature of SiO occurs in the spectrum even

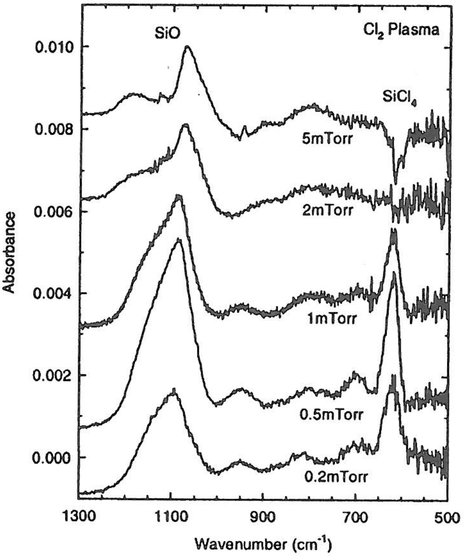

Fig. 3 FTIR absorption spectra in the gas phase during ECR plasma etching of Si in Cl_2 at different pressures P_0.

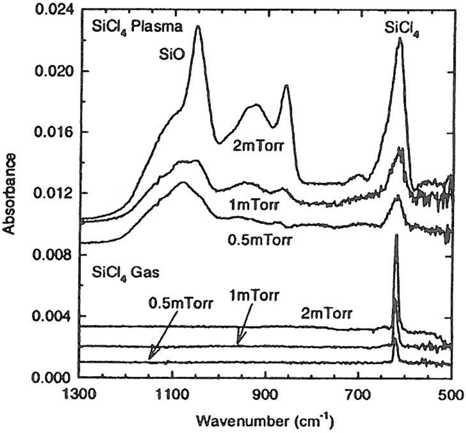

Fig. 4 FTIR absorption spectra of pure $SiCl_4$ gases and plasmas at different pressures P_0.

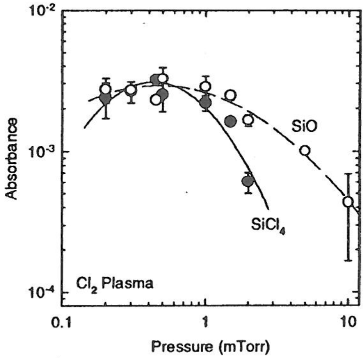

Fig. 5 Peak absorbances of the 620-cm^{-1} $SiCl_4$ and 1100-cm^{-1} SiO bands as a function of pressure P_0 during ECR plasma etching of Si in Cl_2.

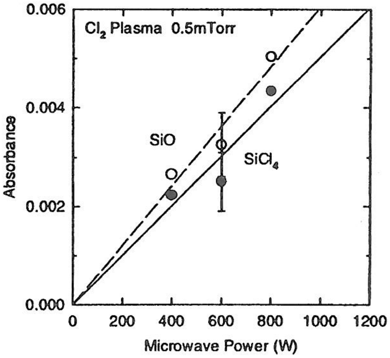

Fig. 6 Peak absorbances of the 620-cm^{-1} $SiCl_4$ and 1100-cm^{-1} SiO bands as a function of microwave power at P_0=0.5 mTorr.

at P_0>2 mTorr, with its peak position shifting toward lower frequencies. A similar peak shift of the SiO absorption feature at high pressures is also seen in the spectrum of pure $SiCl_4$ plasmas shown in Fig. 4.

Figure 5 shows the peak absorbance of the 620-cm^{-1} band of $SiCl_4$ as a function of pressure P_0, together with that of the 1100-cm^{-1} band of SiO, measured in the gas phase during ECR plasma etching of Si in Cl_2. The P_0 dependence of the absorbance of $SiCl_4$ is different from that of SiO, as mentioned above; the P_0 dependence of the Si etch rate obtained tended to be similar to the latter [15]. In contrast, the dependences of the two absorbances on incident microwave power were very similar, as shown in Fig. 6 at a fixed P_0=0.5 mTorr. These results may reflect the difference between reaction processes for $SiCl_4$ and SiO, but the details are not understood at present. Figure 7 shows the peak absorbance of the 620-cm^{-1} $SiCl_4$ band as a function of pressure P_0 in pure $SiCl_4$ gases. The absorbance exhibits an approximately linear increase with increasing P_0. By comparing the results in Figs. 5 and 7, where the vertical scales of absorbance are relative to each other, it is suggested that during Si etching in ECR Cl_2 plasmas, the concentrations of $SiCl_4$ or etch product species in the discharge are comparable to the feedstock Cl_2 gas densities, e.g., $[SiCl_4] \sim 1\times10^{13}$ cm^{-3} at P_0 =0.5 mTorr. Regarding SiO or silicon oxides, there is no gas sample to be compared. Thus, the absolute concentrations of SiO were estimated from the integrated absorbance A of the 1100-cm^{-1} absorption feature, along with the integrated absorption coefficient k for SiO [10]: at P_0=0.5 mTorr, e.g., $[SiO]=A/\ell k \sim 8\times 10^{11}$ cm^{-3}, or more than one order of magnitude lower than $[SiCl_4]$ and $[Cl_2]$.

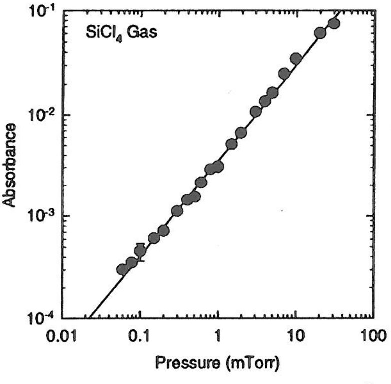

Fig. 7 Peak absorbance of the 620 cm^{-1} band of $SiCl_4$ as a function of pressure P_0 in pure $SiCl_4$ gases.

Figure 8 shows typical IR-RAS spectra on the surface in the range 1300−500 cm^{-1}, observed during and after ECR plasma etching of Si in Cl_2 at a pressure of P_0=0.5 mTorr. It is noted here that on the surface, the absorption spectrum in the range 650−500 cm^{-1} is markedly different from that in the gas phase; the unresolved features at lower frequencies may be assigned to unsaturated silicon chlorides $SiCl_x$ (x=1−3), referring to the IR transmission absorption spectrum of porous silicon films after saturation exposure of chlorosilanes [14]. Thus it is suggested that unsaturated $SiCl_x$ (x=1−3) as well as $SiCl_4$ occurred on the etched surface. The absorption peak corresponding to $SiCl_4$ is more clearly seen after etch run. Additionally, on the surface, two more absorption features appear around 1100 and 800 cm^{-1}, corresponding to the asymmetric stretching and the bending vibrational modes of Si-O, respectively. Such RAS features on the surface were found to significantly disappear after Ar plasma treatment with additional rf biasing, thus the absorption features observed being attributable to product species formed on the surface as a result of etching reactions.

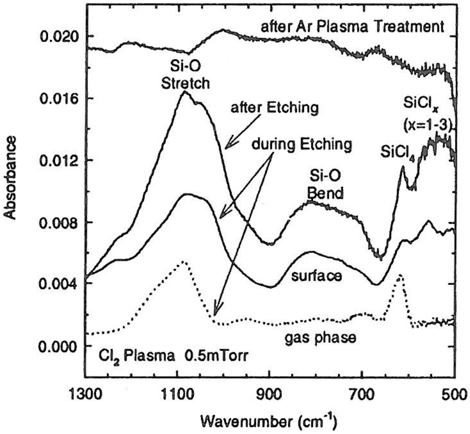

Fig. 8 IR-RAS spectra on the surface during and after ECR plasma etching of Si in Cl_2 at P_0=0.5 mTorr.

In conclusion, *in situ* FTIR absorption spectroscopy has been utilized to detect reaction products in the gas phase and on the surface during ECR plasma etching of Si in Cl_2. Silicon tetrachloride $SiCl_4$ was the primary product species observed in the gas phase, while unsaturated silicon chlorides $SiCl_x$ (x=1−3) were also found to occur on the surface. These results imply that upon desorption from the surface, $SiCl_4$ was formed on or near the surface through reactions between unsaturated $SiCl_x$ (x=1−3) and chlorine atoms or molecules.

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