Evaluation of Growth and Cleaning Rates of Chamber-Wall Deposition during Silicon Gate Etching

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To assure the repeatability of the gate etching process, in situ plasma cleaning is used to remove the deposits on the chamber wall. We studied the mechanism of deposition and cleaning of silicon containing films on the chamber wall formed during silicon etching using the attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). During the silicon etching with a Cl₂/O₂ plasma, a silicon-oxychloride film grows on the chamber wall due to the oxidation of the etch products. In the growth of the deposition films, the oxygen gas plays a key role. In a pure Cl₂ plasma the deposition is removed even while the silicon etching is proceeding on the wafer. It was also found that the deposition rate is square proportional to the O₂ gas flow rate. A simple kinetic model that attributes the square dependence to the consecutive oxidations of the two adjacent dangling bonds of a silicon atom has been described. Then the in situ cleaning of silicon-oxychloride with SF₆ plasma was investigated with regard to the cleaning rate. Although oxygen gas is often added to the cleaning gas so as to remove commonly seen residues such as carbon or sulfur, there is a concern that oxidation may reduce the cleaning rate. It was confirmed that an oxygen addition of 30 sccm to the SF₆ gas of 150 sccm causes insignificant effect. Further study to increase the cleaning rate revealed that lower pressure and larger total gas flow rate are effective. The effect of pressure is understood combined with the change in the plasma density. On the other hand, the total gas flow rate changes the density of etch products near the chamber wall. It was confirmed that the total gas flow rate does not change the etching rate of silicon-oxychloride on the wafer as it lies near the stagnation point of the gas flow.

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I. INTRODUCTION

As the transistor dimensions are shrinking down into a few tens of nanometers, allowable process variations in plasma etching are reducing. In complimentary metal oxide silicon field effect transistors (CMOSFETs), the gate length is the critical dimension for various electrical properties. Also these electrical properties are highly sensitive to such properties as dopant profile and channel stress, which in turn depend on the feature profile of the gate electrode. Therefore precise repeatability of gate etching is indispensable in the fabrication of the gate electrode.

Recently, many works focused on the condition of the plasma chamber wall as a primary source of process fluctuation [1–6]. For the silicon gate etching, Cl₂ or Br-based gas is often used. At low pressure the density of an etchant radical such as Cl or Br is under strong influence of the chamber wall due to the large mean free path and recombination on the wall. Kota et al. revealed that the surface recombination rates of Cl and Br depend on the surface material by their molecular beam experiments [2, 3]. It was also found that the recombination rate changes during a polysilicon etching as a silicon oxide film covers the chamber wall [4]. Therefore the careful conditioning of the chamber wall is indispensable to maintain reproducible etching processes [4–6].

In this study, the attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy is used to analyze the thin deposition films on the chamber wall [7–9]. Recently, Godfrey et al. installed an ATR prism on the chamber wall of inductively coupled plasma (ICP) source to monitor the growth of a silicon oxychloride film on the prism [10]. In a series of following reports using the same monitor, Ullal et al. examined the characteristics of silicon-oxychloride (OSi–Cl) deposition during silicon etching using Cl₂/O₂ plasma [11–14]. They found the enhancement of OSi–Cl growth by oxygen addition and proposed a reaction model of the deposition rate [12]. In the model, it is assumed that the deposition rate is proportional to oxygen flow rate although no experimental data is provided. In the further studies about SF₆ plasma cleaning, they confirmed that fluorination of the OSi–Cl layer propels the cleaning process [13, 14].

In situ plasma cleaning is a common technique to prevent defective particle generation. However, the time consumed for the cleaning process reduces the overall throughput of an etching tool in the high volume manufacturing. Nevertheless the cleaning rate of OSi–Cl layer was not much discussed in the previous papers.

In this study, we have studied the growth and cleaning rates of OSi–Cl layers using the in situ ATR-FTIR monitor installed on a UHF-ECR plasma gate-etcher. The effect of oxygen flow rate on the deposition rate is studied to clarify the deposition mechanism. Then the cleaning rate of the deposition is evaluated so as to improve the throughput of the etching tool.

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II. EXPERIMENTAL

A schematic view of the UHF-ECR plasma etching tool used in this study is shown in Fig. 1. This etching tool is designed most suitable for fine-scale etching of silicon patterns such as gate electrodes. The UHF electromagnetic wave which is guided by a coaxial cable is irradiated from the top of the chamber so as to enter the low pressure plasma chamber through the quartz top plate. The UHF wave generates the plasma just beneath the quartz top plate. The plasma diffuses downward along a vertical axisymmetric divergent magnetic field induced by the surrounding solenoid coils. The RF bias voltage is applied to the wafer stage to accelerate ions toward the wafer. As a result of reactive ion etching, the etch products are emitted from the wafer surface and stick to the chamber wall. The in situ ATR-FTIR sensor is installed on the sidewall of the chamber to monitor the deposition films during etching or cleaning processes. The ATR head is comprised of a ZnSe prism (60 mm long and 20 mm width) and a prism holder for multiple reflections inside as depicted in Fig. 2. The temperature of the chamber and the prism holder are kept at 100°C throughout the following experiments. The temporal variation of the plasma emission is also observed through the quartz window for optical emission spectroscopy (OES).

To study the growth mechanism of the deposition films on the chamber wall, a silicon wafer is etched by the Cl₂/O₂ plasma with UHF power of 400 W and wafer bias power of 17 W at a pressure of 0.4 Pa. The gas flow rate of Cl₂ and O₂ are 100 and 4 sccm, respectively. Once the deposition films are formed on the ZnSe prism and the chamber wall, the absorbance spectrum is measured by the ATR-FTIR monitor. After the measurement, the deposition film is removed by an in situ plasma cleaning process of SF₆/O₂ plasma with the UHF power of 600 W at 1.0 Pa. Typical gas flow rates of SF₆ and O₂ are 150 and 10 sccm, respectively. During the cleaning process a silicon wafer is set on the wafer stage and no wafer bias power is applied. Through these experiments, the ATR-FTIR captures the temporal variations of the deposition films.

Using each absorbance spectrum obtained by the ATR-FTIR, the atomic bonds which comprises the deposition film are studied. For this purpose the spectrum is decomposed into multiple Gaussian distributions. From the center wavenumbers of the Gaussians, the vibration mode of the atomic system and its constituent atoms are identified. The temporal variations in the deposition film are figured using the intensity of the absorbance peaks. Increases or decreases in the absorbance indicate the deposition or the etching of the deposition film on the chamber wall, respectively.

III. RESULTS AND DISCUSSION

A. Analysis of the deposition film on the chamber wall

A typical absorbance spectrum after a silicon etching process is shown in Fig. 3. The spectrum is decomposed into multiple Gaussian peaks. A prominent peak is observed around 1065 cm⁻¹. There is also a group of peaks ranging from 650 to 850 cm⁻¹. The center wavenumbers of the Gaussian peaks are listed in Table I. Various stretching and anti-stretching modes of Si–O–Si and OSi–Cl atomic systems are identified. Most of the vibration modes observed in a-SiO₂ are detected in the absorbance spectrum of the deposition film grown during silicon etching. This result indicates the deposition film is an a-SiO₂ like film including chlorine atoms.

The small peak at 973 cm⁻¹ is not observed in a similar experiment by Ullal et al. [12]. The closest candidate is the Si–OH stretching mode at 980 cm⁻¹ referred in Lang et al. [17]. As no hydrogen atom is contained in the

![FIG. 1: Schematic view of etching tool with the ATR-FTIR and OES monitors.](http://www.sssj.org/ejssnt/)

![FIG. 2: Detail of the ATR head installation on chamber wall.](http://www.sssj.org/ejssnt/)

<table>
<thead>
<tr>
<th>Type</th>
<th>Center wavenumber [cm⁻¹]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si–O–Si AS1 LO</td>
<td>1261</td>
<td>[15]</td>
</tr>
<tr>
<td>Si–O–Si AS1 TO</td>
<td>1065</td>
<td>[15]</td>
</tr>
<tr>
<td>Si–O–Si AS2 LO</td>
<td>1139</td>
<td>[15]</td>
</tr>
<tr>
<td>Si–O–Si AS2 TO</td>
<td>1195</td>
<td>[15]</td>
</tr>
<tr>
<td>Si–O–Si SS LO</td>
<td>820</td>
<td>[15]</td>
</tr>
<tr>
<td>Si–O–Si SS TO</td>
<td>808</td>
<td>[15]</td>
</tr>
<tr>
<td>OSi–Cl</td>
<td>748</td>
<td>[12, 17]</td>
</tr>
<tr>
<td>OSi–Cl</td>
<td>692</td>
<td>[12, 17]</td>
</tr>
<tr>
<td>Unidentified</td>
<td>973</td>
<td>[17]</td>
</tr>
</tbody>
</table>

TABLE I: Identification of Gaussian peaks in Fig. 3. The center wavenumbers of the peaks are shifted for Gaussian fitting. AS and SS mean anti-symmetric and symmetric stretching, LO and TO mean longitudinal and transverse optics, respectively [15].
FIG. 3: Gaussian decomposition of the absorbance spectrum observed with ATR-FTIR after silicon etching by Cl₂/O₂ plasma. Circled markers are experimental results and thin lines are Gaussian constituents. The detail of the peak identifications is described in Table I.

TABLE II: Identification of Gaussian peaks in Fig. 4. The center wavenumbers of the peaks are shifted for fitting. AS and SS mean anti-symmetric stretching and symmetric stretching, respectively.

<table>
<thead>
<tr>
<th>Type</th>
<th>Center wavenumber [cm⁻¹]</th>
<th>Han et al. [18]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₃Si₁₋₂Si–F</td>
<td>892</td>
<td>890</td>
</tr>
<tr>
<td>O₂Si–F₂ (SS)</td>
<td>924</td>
<td>920</td>
</tr>
<tr>
<td>O₂Si–F</td>
<td>958</td>
<td>950</td>
</tr>
<tr>
<td>O₂Si–F₂ (AS)</td>
<td>999</td>
<td>990</td>
</tr>
</tbody>
</table>

feed gas of our experiment, the identification of this peak remains ambiguous.

B. Cleaning of silicon-oxide film on the chamber wall

In the in situ cleaning, the silicon-oxychloride film is exposed to the SF₆/O₂ plasma. As a result of fluorination the absorbance spectrum changes drastically as shown in Fig. 4. The spectrum basically has a similar shape as the one observed in the previous works with other plasma sources[13, 18]. The identifications of the Gaussian peaks of the fluorinated deposit are summarized in Table II. The elimination of OSi–Cl peaks and the emergence of OSi–F peaks imply that the Cl atoms bonded to the surface Si are replace by F atoms. Also the prominent peak of the AS₁ mode at 1065 cm⁻¹ is reduced relative to the AS₂ mode. In AS₁ mode the O atoms vibrates in phase with each other. On the other hand, in the AS₂ motion the adjacent O atoms move in the opposite direction [15]. Probably the segmentation of SiO₂ atomic system by fluorination suppresses the systematic vibration of AS₁ mode.

Figure 5 shows the changes in the Si–O and Si–F absorbance during the cleaning process of wall deposit. The Si–O absorbance is calculated as the average of the absorbance intensity between 1000 and 1200 cm⁻¹. In the same way, the Si–F absorbance is evaluated using the averaged intensity between 900 and 1000 cm⁻¹. The solid line shows the optical emission intensity of SiF at 440 nm.

Before the ignition of plasma, only the silicon-oxychloride film is detected as the SiO absorbance. After the ignition of SF₆ plasma, the SiO absorbance gradually starts to decrease, while the Si–F absorbance…

FIG. 4: Gaussian decomposition of the absorbance spectrum observed with ATR-FTIR during SF₆/O₂ plasma cleaning of the deposition layer in Fig. 3. Circled markers are experimental results and thin lines are Gaussian constituents. Detail of the peak identification is described in Table II.

FIG. 5: Fluorination and removal of the silicon-oxychloride deposition during SF₆ plasma cleaning. Lines with markers are the peak heights of SiO and SiF. Emission intensity of SiF at 440 nm is obtained by OES.
rapidly increases indicating fluorination of the silicon-oxychloride [14]. The fluorination saturates after 10 seconds of plasma exposure. Then the cleaning rate reaches steady state where the absorbance curves show a straight decline. Even after the disappearance of the absorbance, the optical emission of SiF remains. The SiF radical is produced by the electron impact dissociation of SiF$_2$ or SiF$_4$, which are the major products of silicon etching by F radicals [19]. During the steady state of the cleaning from 35 to 45 seconds, the emission of reaction products should be unchanged. However, the optical emission of SiF is constantly decreasing throughout the cleaning. A plausible explanation is a distributed thickness of deposition film along the chamber wall. The continuous decrease in the remaining deposition area is probably the reason of the SiF emission behavior.

C. Deposition rate and growth mechanism of wall deposit on the chamber wall

A deposition layer grows on the chamber wall due to the oxidation of the etch products [12]. To investigate the effect of oxygen gas further, temporal variations of the Si-O absorbance during silicon etching was observed at various oxygen gas flow rates. The experimental results are shown in Fig. 6 where the flow rate of Cl$_2$ is fixed at 100 sccm and the O$_2$ flow rate is set at 0, 1, 2, 3, and 4 sccm. The time dependence is mostly linear for each O$_2$ flow rates, indicating that the deposition rates are constant. The growth of silicon-oxychloride film is largely enhanced by oxygen gas. There can be seen no deposition without O$_2$ gas. Instead, another experimental result shown in Fig. 7 reveals that the deposition film is removed from the chamber wall in a pure Cl$_2$ plasma during a silicon etching. On the other hand, the absorbance for 1 sccm of O$_2$ gas addition in Fig. 6 shows a growth of the deposition film. Even a slight addition of O$_2$ gas turns an etching of the silicon-oxychloride film into a deposition.

To see the change in the O radical density in the plasma, the optical emission intensities of O radicals at 777.2 and 844.6 nm [21] are shown in Fig. 8(a). If a small addition of O$_2$ gas does not change the electron temperature and plasma density, these optical emission intensities are proportional to the O radical density. Considering the linearity of the two oxygen lines in Fig. 8(a), the O radical density seems to be proportional to the O$_2$ flow rate. However, the deposition rates calculated from the slopes of absorbance are square proportional to the O$_2$ gas flow rate as shown in Fig. 8(b). There should be an explanation why the linear increment in O radicals leads to the deposition rate square proportional to the O$_2$ flow rate.

A brief deposition model just enough to explain the observed square dependence on the oxygen gas flow rate is shown in Fig. 9. It is assumed that an average silicon atom on the surface has two dangling bonds and is anchored to the surface with two bonds bounded to the surface O atoms. The dangling bond of Si on the surface can be occupied by O, Si, or Cl radicals. The bond energies of Si-O, Si-Si, and Si-Cl are 452, 222, and 381 kJ/mol, respectively. The Si-O bond once formed contributes to the continuous growth of the deposition. The Si-Si bond is replaced by a Si-O or Si-Cl bond since its bond strength is weak. As the Si-Cl bond is relatively strong compared with a Si-O bond, it terminates the formation of SiO$_2$ network. The Si-Cl bond remains to form a silicon-oxychloride film which is detected as the absorbance peak of OSi–Cl. In the first step in Fig. 9(a), a dangling bond of a silicon atom is taken by an O radical. Approximately the coverage of Si-O bond on the surface is proportional to the O radical density. For the continuous growth of the deposition, the adjacent dangling bond of the Si-O bond should be occupied by an O radical too. The probability of an O radical occupying the site in spite of the competition with the other radicals is also proportional to the O radical density. As a result, the deposition rate seems to be proportional to the square of the O$_2$ gas flow rate.

![FIG. 6: Temporal variation in the SiO absorbance during the silicon etching by Cl$_2$/O$_2$ plasma at 0.4 Pa. The Cl$_2$ flow rate was fixed at 100 sccm.](http://www.sssj.org/ejssnt/)

![FIG. 7: Removal of the silicon-oxychloride deposition in pure Cl$_2$ plasma during silicon etching with a wafer bias power of 17 W.](http://www.sssj.org/ejssnt/)
FIG. 8: Effect of O₂ addition: (a) the emission intensities of O radical at 777.2 nm and 844.6 nm, (b) deposition rate depending on O₂ flow rate. Circles are calculated from absorbance and the solid line is parabolic fitting curve to the experimental results.

D. Evaluation of cleaning rate

To keep productivity of a gate etching tool, SF₆/O₂ plasmas are frequently used for in situ cleaning. Dissociation of SF₆ in the plasma provides F radicals to remove the depositions on the chamber wall. Simultaneously O radicals remove commonly seen residues such as carbon and sulfur. Effective design of in situ cleaning is indispensable to satisfy both of reproducibility and throughput of an etching tool. In the subsequent experiments, we investigate the impact of process conditions on the cleaning rate of SF₆/O₂ plasma. To prepare the initial deposition films, the etching of a silicon wafer by Cl₂/O₂ plasma precedes each cleaning experiment. Then the decrease in the absorbance of SiO₂ during the SF₆ plasma cleaning is monitored by the ATR-FTIR.

Meanwhile the addition of oxygen invokes a concern that O radicals may prevent the cleaning reactions of silicon-oxychloride films. To study the effect of oxygen, cleaning rates are observed at the O₂ flow rates of 0, 10, and 30 sccm. The result in Fig. 11 shows that the cleaning rate is slightly faster when SF₆ plasma is used with less oxygen. Although O radicals in the plasma can inhibit fluorination of silicon surface by oxidation, the effect is insignificant with this amount of oxygen additions.

Next the effect of gas pressure is investigated. The SF₆ plasma cleaning without oxygen is executed at 0.4, 1.0, and 1.6 Pa. The flow rate of SF₆ is set at 150 sccm. The cleaning rate calculated from the gradients of absorbance is shown in Fig. 11. Also shown is the etching rate of silicon oxide measured with a wafer prepared with a TEOS (Tetraethyl Orthosilicate) process. For the experiment, the wafer bias voltage is not applied. The both rates are
FIG. 10: Temporal variation of SiO absorbance during the in situ SF₆ plasma cleaning. The flow rate of SF₆ is 150 sccm and the pressure is 1.0 Pa.

FIG. 11: Dependence of the cleaning and etching rates on the pressure. The etching rate is calculated from the gradient of the SiO absorbance curve in the SF₆ plasma where the flow rate of SF₆ is 150 sccm. The etching rate is measured with the etching of a silicon oxide (TEOS) wafer in the SF₆/O₂/Ar plasma. The gas flow rates of SF₆, O₂, and Ar are 100, 20, and 27 sccm, respectively.

FIG. 12: Effect of total flow rate. The cleaning rate is calculated from the gradient of the absorption curve. The cleaning rate is measured in SF₆ plasma at 1.0 Pa. The compared etching rate of the wafer is the averaged values across a silicon oxide wafer. The etching rate is for a silicon oxide wafer in SF₆/O₂/Ar plasma at the flow rate ratio of 15:4:3.

Translated as the etching rates of the silicon oxide films at different positions in the chamber; the cleaning rate is at the chamber sidewall, and the etching rate at the wafer stage. Both the cleaning and etching rates are higher at lower pressures. This seems to be a result of the increase in plasma density. In an ECR (Electron Cyclotron Resonance) plasma, the plasma density increases at low pressure where electron heating by ECR is not interrupted by collisions with the background neutral molecules [20].

Finally, the effect of total flow rate is studied. The solid circles in Fig. 12 show the cleaning rates which are calculated from the gradient of the SiO absorbance curves. The increase in the cleaning rate with the total flow rate is eminent. The cleaning rate at 150 sccm of SF₆ is twice of that at 50 sccm. In contrast the etching rate of a silicon oxide wafer hardly depends on the total flow rate. Although the process conditions are slightly different to compare the cleaning and etching rates, it is distinctive that the etch rate on the wafer is insensitive to the total gas flow rate.

In order to understand the result in Fig. 12, the changes in the radical densities are examined using optical actinometry [21, 23]. Ar gas is added to 20% of the total flow rate for actinometry. Then the optical emissions of Ar at 811.5 nm, F at 703.7 nm, and SiF at 440 nm (denoted as Iₐr, Iₐ, and Iₛᵢ₉, respectively) are observed by the OES monitor. Changes in F and SiF radical densities are estimated from Iₐ/Iₐᵣ and Iₛᵢ₉/Iₐᵣ. The SiF radical is used to estimate the behavior of etch products.
such as SiF$_2$ or SiF$_4$. The result in Fig. 13 suggests that F radical density suffers negligible effect of the total gas flow rate. On the other hand, the increase in the total flow rate causes a significant decrease in the SiF radical density. The plunge in the SiF radical density is due to the reduced residence time of the etching products in the plasma chamber. Since SiF radicals stick to the chamber wall and consequently slow down the cleaning process, the decrease in SiF radicals at the high flow rates results in the high cleaning rate. However, it has been pointed out that the etch product density close to the wafer does not change much by total gas flow rate[22] since the center of the wafer is the stagnation point for the gas flow incoming from the top gas inlet. This explains the unchanged etching rate on the wafer in Fig. 12.

**IV. CONCLUSION**

The growth and cleaning mechanisms of the deposition films on the chamber wall during a silicon etching process was investigated using the ATR-FTIR and OES monitors installed on a UHF-plasma gate etching tool. After a silicon etching with a Cl$_2$/O$_2$ plasma, the absorbance peaks of SiO$_2$ and OSi–Cl were detected. The peaks identified by the Gaussian decomposition are similar to those observed in the previous works of the other authors, indicating that the chemical structure of the deposition resembles to the thermal oxide [15] or the silicon oxides formed in the other types of plasma chambers [10, 12].

It was confirmed that oxidation of etching product is indispensable for the growth of the deposition since a pure Cl$_2$ plasma removes the wall deposition even during a silicon etching process. The deposition rate calculated from the SiO$_2$ absorbance is square proportional to the O$_2$ flow rate up to 4 percent addition to Cl$_2$ gas. A simple kinetic model which could explain the result was illustrated.

Then, we investigated cleaning rates of the in situ cleaning with SF$_6$/O$_2$ plasma. With 150 sccm of SF$_6$ gas flow, the oxygen addition up to 30 sccm affected the cleaning rate insignificantly despite the concern of oxidation. At lower pressure conditions the cleaning rate is increased probably due to the increase in the plasma density. Moreover increasing the total gas flow rate is also effective to improve the cleaning rate. Although the cleaning rate observed at the chamber wall by ATR-FTIR is higher at the larger total gas flow rate, the etch rate of silicon oxide on the wafer is unchanged. From the analysis of optical emission, the etch product density near the surface can explain the opposite effect of total gas flow rate.

In this study, a quantitative optimization of in situ cleaning is efficiently performed using the ATR-FTIR monitor. Understanding of the dependence of deposition and cleaning rates on the process conditions enables us to design a stable etching sequence which alleviates the effect of the chamber wall.