A New Diagnostic Technique for Monitoring Plasma Reactor Walls: Multiple Total Internal Reflection Infrared Surface Probe

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Acknowledgements: This research is funded by the Lam Research Corporation and the California Semiconductor Manufacturing Alliance for Research and Training (SMART) Program.
Chemically Reactive Gas Plasmas for Etching

\[
\begin{align*}
\text{Cl}_2 + e^- &\rightarrow \text{Cl}_2^+ + 2 \text{e}^- \\
\text{Cl}_2 + e^- &\rightarrow 2 \text{Cl} + \text{e}^- \\
\text{Cl} + e^- &\rightarrow \text{Cl}^* + \text{e}^- \\
\text{Cl}^* &\rightarrow \text{Cl} + h\nu
\end{align*}
\]

Induction Coil

rf Bias

Power

Sheath

\[\Delta V = 10 - 1000 \, \text{V} \]
\[d_s = 0.1 - 0.01 \, \text{cm}\]
Motivation and introduction: the need for a “wall probe”

- Plasma reactor walls can play a crucial role in determining the plasma properties, such as the radical concentrations and ion densities, especially at low pressures.

- This well-known plasma-wall interaction has caused problems ranging from process drifts in IC manufacturing to irreproducible data in fundamental studies employing plasma diagnostics.

- Terms such as “wall conditioning” and “reactor seasoning” have become accepted language in literature to describe art of avoiding such effects.

- There are no diagnostic techniques to quantify the chemical state of the walls in a plasma reactor.
Objective

- Develop a surface probe based on multiple total internal reflection Fourier transform infrared (MTIR-FTIR) spectroscopy that can be used as a diagnostic tool to monitor films and adsorbates on walls of a plasma etching reactor (Lam TCP 9400®).

- Demonstrate applications of the probe
  - Effect of wall conditions on Cl/Cl₂ concentrations and uniformity of etching.
  - Monitoring deposits on reactor walls during Cl₂/O₂ etching of Si.
  - Monitoring efficacy of chamber wall cleaning in Shallow Trench Isolation (STI) etching.
  - Monitoring wafer-to-wafer reproducibility of wall conditions and its effect on process reproducibility.
Experimental Setup - Lam TCP 9400
MTIR-FTIR Wall Probe

Perspective view

Top view of the optical box

E = E₀ exp \{-z/d_p\}

From FTIR Spectrometer

To HgCdTe Detector

Chamber Wall

Internal Reflection Element

Plasma

IR beam from FTIR Spectrometer

IR beam to Detector

Optical Box

Wafer

Plasma

Reactor chamber

n₁

E

z

A

n₂

d
Principles of MTIR-FTIR

- Film is probed through attenuated total reflection mode if $n_f < n_{IRC} \sin \theta$.

- Film is probed through multiple internal transmission mode if $n_f > n_{IRC} \sin \theta$.

- Surface species are probed through attenuated total reflection.

\[ E = E_0 \exp \left\{ -\frac{z}{d_0} \right\} \]
Principles of MTIR-FTIR
Shallow Trench Isolation (STI) process is used to isolate transistors in ICs. In STI process trenches with tapered sidewalls are etched into Si using Cl₂/O₂. While Cl₂ etches Si anisotropically, O reacts with reaction products (SiClₓ 0≤x≤4) to deposit a silicon oxychloride (SiOₓClᵧ) film on the sidewalls. The feature profile shape depends on a delicate balance between etching and deposition.
SiO$_x$Cl$_y$ film is deposited not only on the trench sidewalls but also on the reactor walls.

Presence of the SiO$_x$Cl$_y$ film on the wall affects the radical wall recombination probabilities.

SiO$_x$Cl$_y$ film must be etched from the reactor walls using SF$_6$ containing plasma in between every wafer. This cleaning process is referred to as Waferless Auto Clean (WAC).
Cl and Cl₂ concentration measurements

- Effect of the wall conditions on the absolute Cl and Cl₂ concentrations were determined using optical emission spectroscopy in conjunction with actinometry as described by Donnelly and Malyshev. (J. Vac. Sci. Technol. A 14, 1076, 1996; J. Appl. Phys. 84, 137, 1998)

\[
\frac{n_i}{n_{Ar}} = \alpha_i(T_e) \frac{I_i}{I_{Ar}}
\]

- Used 306 nm Cl₂, 822 nm Cl and 750.4 nm Ar emissions and corrected for the Te dependance of α.

- Calibrated α using as power → 0, dissociation → 0, nₐCl₂ → n₉ = P₉/kₐT₉

- Used a simple model of the Cl mass balance with an adjustable Cl surface recombination probability, γ.

\[\text{Cl}_2 + e^- \xrightarrow{k_d(T_e)} 2 \text{Cl} + e^- \]

\[\text{Cl} + \text{wall} \xrightarrow{\gamma} \frac{1}{2} \text{Cl}_2 \]

\[\text{Cl} \xrightarrow{s_p} \text{pumped out} \]
Drift in Cl concentration is due to changes in the Cl recombination probability on the walls. The drift is not related to chamber temperature, charge density or $kT_e$

Exposure to SF$_6$/O$_2$ plasma resets the walls to a reproducible condition.
Reseting the chamber walls through “cleaning” with SF$_6$ plasma is essential for collecting reproducible data.

- Cl concentration exhibits hysteresis with plasma power due to changes in the Cl recombination probability on the chamber walls with time.
A thin SiO₂ film deposited on the chamber walls decreases Cl surface recombination probability, $\gamma$

- ~5 Å thick SiO₂ film is deposited on reactor walls even when Si wafer or O₂ are not present in the chamber: quartz window is the source of Si and O.

- Wall recombination probability of Cl is lowered drastically when walls are coated even with ~ a monolayer of SiO₂.

- $\gamma$ calculated by fitting measured Cl concentration to a model is ~0.03 on SiO₂ covered walls.

- SF₆/O₂ plasma removes the SiO₂ film.

- $\gamma$ ~1 after the SiO₂ is removed.
Cl₂ dissociation under identical plasma operating conditions can be drastically different depending on the wall conditions.

**No chamber reset: SiO₂ on walls**
- Cl loss from the reactor is limited by wall recombination.
- High % dissociation, low γ.
- % dissociation depends on pressure.

\[
  n_{\text{Cl}_2} = \frac{n_g}{1 + \frac{8k_d n_e V_d}{S \gamma_{\text{Cl}} + 4S_p}}
\]

**With chamber reset**
- Cl loss from the reactor is limited by transport (diffusion to the walls).
- Low % dissociation, higher γ.
- % dissociation is independent of pressure.

\[
  n_{\text{Cl}_2} = \frac{n_g}{1 + \frac{8k_d n_e V_d}{V_d D/\Lambda^2 + 4S_p}}
\]
Cl concentration drifts slowly as the reactor walls are covered with a thin layer of SiO$_2$ and $\gamma$ decreases.
Effect of a thin SiO$_2$ film on the walls (and the resulting change in the Cl recombination probability) on Si etching uniformity

0 min.  
After 5 min.  
After 10 min.  
After 15 min.  
After 20 min.  
After 25 min.

50 mTorr, 150 sccm Cl$_2$, 600 W TCP power, 100 W rf-bias
Plasma Etching Uniformity with WAC
(SF₆ plasma cleaning in between wafers)

- Removal of the silicon oxychloride with SF₆ resets the reactor wall back to the reproducible condition.
- Etch rate and uniformity return to their initial values.
Detection of adsorbed SiCl<sub>x</sub> etch products on the reactor walls during Si etching with Cl<sub>2</sub> plasma using the MTIR-FTIR surface probe

- **Experiment:**
  - Start with ~20 Å thick SiO<sub>2</sub> film on the MTIR crystal.
  - Turn on a Cl<sub>2</sub> plasma with Si wafer in the reactor but without rf bias applied to the chuck ⇒ no etching ⇒ no SiCl<sub>x</sub>
  - Turn on the rf bias: Si wafer etches at 4000 Å/min.

- SiCl<sub>x</sub> absorptions are not observed after step 2 ⇒ Cl does not adsorb easily on SiO<sub>2</sub> surface. This is consistent with low γ.

- SiCl<sub>x</sub> absorptions observed after step 3 ⇒ SiCl<sub>x</sub> adsorbed onto the wall are produced by etching reactions.
Deposition of $\text{SiO}_x\text{Cl}_y$ film on the walls during $\text{Cl}_2/\text{O}_2$ etching of Si

- During $\text{Cl}_2/\text{O}_2$ etching of Si, $\text{SiCl}_x$ etch products react with O and deposit a chlorinated $\text{SiO}_2$ ($\text{SiO}_2:\text{Cl}$) film on the chamber walls.
Effect of bias power on chamber wall deposition

Under otherwise similar etching conditions, an increase in bias power, increases the etch rate and hence the SiCl\textsubscript{x} production.

Increasing SiCl\textsubscript{x} production causes an increase in deposition on the chamber walls ⇒ chamber wall deposition depends on amount of SiCl\textsubscript{x} etch products generated.
Effect of oxygen on chamber wall deposition

Under otherwise similar etching conditions, and constant total flow rate an increase in O₂ inlet flow, increases the deposition on the chamber wall.

At higher O₂ flows, wall deposition decreases because etch rate decreases (SiClₓ limited), until etching finally stops and there is no deposition on the chamber walls.
Sufficiently long SF₆/O₂ plasma (WAC) removes the SiO₂:Cl deposits.
F abstracts and replaces Cl in the SiO$_2$:Cl film converting it to SiO$_2$:F

- Si-F stretching absorption initially increases during SF$_6$/O$_2$ plasma cleaning as F abstracts and replaces Cl in the SiO$_2$:Cl film. It undergoes a maximum and decreases as the film is removed.
- Si-O peak shifts to high wavenumber after Cl$_2$/O$_2$ etching of Si.
- If the SF$_6$/O$_2$ WAC step is short, the wall deposits are not removed completely and F incorporated into the film could leach out in next processing step.
- SiF$_4$ is detected in the reactor exhaust and in the plasma even though no fluorine containing species are introduced into the chamber.

- The decay in the SiF$_4$ concentration in the exhaust indicates that an exhaustible amount of F is present in the reactor.

- F trapped in the SiO$_2$ walls as well as in the quartz window during SF$_6$/O$_2$ plasma cleaning step is released into the plasma in the subsequent steps.
10 wafers etched with Cl₂/O₂ plasma with cleaning (WAC) of the walls in between each wafer.

Etch rate is very reproducible.

Reproducible wall conditions ensured by the WAC: SiOₓClᵧ film is completely removed during WAC.

However, close observation of the trench profiles show a subtle drift in the slope of the sidewalls.
Etch Profile Drift

After etch | Stripped
---|---
Wafer 1 | Wafer 10

- Amount of deposition on the trench sidewalls decreases from wafer 1 to wafer 10 ⇒ sidewall angle increases.
Infrared spectra collected after etching each wafer show that the amount of film deposited on the walls increases even though the walls are cleaned completely between etching steps and etch rate is constant.

This trend is opposite that of the deposition on the trench sidewalls.
With every successive wafer processed in the chamber:
- the amount of wall deposition due to each wafer increases;
- emission from SiClₓ etch products increase;
- etch rate and SiCl₄ concentration in reactor exhaust remain constant;
- deposition on the trench sidewalls decrease.

Other experiments show that the drift is related to the amount of residual F in the reactor, most likely trapped F in the quartz window.

We still do not understand the detailed mechanism of the drift and the role of residual F.
The amount of etch products leaving the bottom of the trench is **not changing**.

- Gas phase $\text{SiCl}_x$ species concentration **increases**.
- Deposition on chamber wall **increases**.
- Etch product deposition on sidewall of trench **decreases**.
- Amount of SiF₄ in exhaust of the reactor indicates the residual Fluorine level in the chamber.
- More Fluorine is incorporated in the chamber when multiple WAC steps are run.
- Fluorine level in the chamber is **not replenished** to the same level by the succeeding clean-1.
- Residual Fluorine level in the chamber **decreases** as more wafers are processed in the chamber and finally reaches a steady state.
Fluorine level maintained - No wafer-to-wafer drift

- Fluorine level in the chamber is replenished to the same level by the succeeding Clean-2’s.
- Residual Fluorine level in the chamber is constant as more wafers are processed in the chamber.
- Deposition on the chamber wall is not changing.
- Deposition on the sidewalls of the trench is also invariant.
Fundamental Understanding of Plasma-Wall Interactions and Managing Wall Conditions Reduces Wafer-to-Wafer CD Variability

- Gate Etching Process with WAC Every Wafer

<table>
<thead>
<tr>
<th>Variation (nm 3sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>run-to-run 3sigma (with WAC)</td>
</tr>
<tr>
<td>run-to-run 3sigma (w/o WAC)</td>
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</tbody>
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Net within Wafer CD Bias (with WAC every wafer)

Data Courtesy of H.K. Chiu and H.J. Tao Taiwan Semiconductor Manufacturing Company, Taiwan
A novel diagnostic technique based on multiple total internal reflection (MTIR) FTIR has been developed and used to monitor wall conditions during plasma etching of Si with Cl\textsubscript{2}/O\textsubscript{2} plasmas.

This new probe was used to develop a detailed and fundamental understanding of the interactions between the plasma and the reactor walls.

Fundamental understanding of plasma-wall interactions obtained through MTIR-FTIR and other plasma diagnostics were used to

- Improve wafer-to-wafer reproducibility
- Optimize wall cleaning processes
- Minimize wall cleaning time to decrease emissions