II. Zero-dimensional model. The "plasma dimension". Silane depletion. Importance of gas composition in the plasma.

III. Electromagnetic uniformity: finite RF wavelength in large area, VHF reactors.

IV. Uniformity in time: rapid equilibration to steady-state process parameters. Direct pumping of a plasma reactor.

V. So where is the problem? - Causes of non-uniformity. Some recommendations.
An example: Hydrogen dilution for plasma deposition of $\mu$-c-Si:H

Low silane concentration $c = \frac{\Phi_{\text{SiH}_4}}{\Phi_{\text{total}}} < 5\%$ is commonly used.

Silane

Hydrogen
Reason for hydrogen dilution

Need high ratio of H to SiH$_x$ fluxes to deposit $\mu$-c-Si:H

"Add more hydrogen than silane"

Intuitively

Selective etching model

Chemical annealing model

Surface diffusion model

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...but the optimal plasma control parameters are less clear
...because the plasma is complex.

{molecules} $\Phi_{\text{H}_2}$ $\Phi_{\text{SiH}_4}$

{electron diss$^n$: $n_e$, $T_e$} $\text{SiH}_x$, $\text{H}$, cations, anions

{sec$^y$ reactions} polysilanes, dust

{transport in the plasma and the sheath}

{surface reactions} $\downarrow$ $\text{SiH}_x$ $\text{H}$, $\text{H}_2$ $\uparrow$

$P_{\text{RF}}$[W] $f$ [MHz] $\text{H}_2$ $\text{SiH}_4$, polysilanes, dust

$\rho_{\text{process}}$
Consider low pressures (< 2 mbar)

- $\Phi_{H_2}$
- $\Phi_{SiH_4}$
- $P_{RF}[W]$,
- $f$ [MHz]

- {molecules}
- $H_2$
- $SiH_4$

- {electron diss$^n$: $n_e$, $T_e$}

- SiH$_x$, H, cations, anions

- {transport in the plasma and the sheath}

- {surface reactions}

- $SiH_x$, H, $H_2$

- H$_2$, SiH$_4$
Consider only the majority species

All reactive species (SiH$_x$, H, and ions) have very low density because of their volume and surface reactions.

- H$_2$ and SiH$_4$ have the dominant partial pressures in the plasma reactor.
- Only H$_2$ and SiH$_4$ leave the plasma reactor.
- The partial pressure of SiH$_4$ (and H$_2$) is ~the same in the pumping line as in the plasma.

"The plasma composition (and deposition) is determined by the partial pressures of SiH$_4$ and H$_2$ in the plasma."
How to measure the silane partial pressure in the plasma?

"inaccessible" plasma reactor

load lock

gate valve

substrate loading door

load lock

gate valve

substrate loading door

vacuum chamber

plasma box
  • heated
  • closed
  • showerhead

pumping line

butterfly valve

process pumps

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Fourier transform infrared (FTIR) absorption spectroscopy via ZnSe windows.
Silane partial pressure measurement

- **a)** Silane infrared absorbance;  **b)** Integrate spectrum;  **c)** Read off a calibrated curve

- Silane pressure with plasma < silane pressure without plasma, due to electron dissociation of silane (irreversible loss).

- Hydrogen partial pressure increases with plasma (silane dissociation product, surface association, & pump speed adjustment)
Silane input concentration (*without* plasma)

\[ \Phi_{\text{H}_2} \quad \Phi_{\text{SiH}_4} \]

\[ p_{\text{SiH}_4}^0 + p_{\text{H}_2}^0 = p_{\text{process}} \]

Define

silane input concentration, \( c = \frac{p_{\text{SiH}_4}^0}{p_{\text{process}}} = \frac{\Phi_{\text{SiH}_4}}{\Phi_{\text{total}}} \)

Note \( 0 \leq c \leq 1 \)
Silane concentration with plasma

\[ p_{\text{SiH}_4} + p_{\text{H}_2} = p_{\text{process}} \]

Define

silane concentration with plasma, \( c_{\text{pl}} = \frac{p_{\text{SiH}_4}}{p_{\text{process}}} \)

silane input concentration, \( c = \frac{p_{\text{SiH}_4}^0}{p_{\text{process}}} \)

same pressure by feedback adjustment to throttle valve
Silane depletion due to plasma

\[ \Phi_{H_2} + \Phi_{SiH_4} = \rho_{process} \]

Define

silane fractional depletion, \( D = \frac{p_{SiH_4}^0 - p_{SiH_4}}{p_{SiH_4}^0} \)

Note \( 0 \leq D \leq 1 \)

silane concentration with plasma, \( c_{pl} = \frac{p_{SiH_4}}{\rho_{process}} \)

silane input concentration, \( c = \frac{p_{SiH_4}^0}{\rho_{process}} \)
Silane concentration in plasma

Therefore

silane concentration in plasma, \( c_{pl} = c(1-D) \)

silane fractional depletion, \( D = \frac{p_{SiH_4}^0 - p_{SiH_4}}{p_{SiH_4}^0} \)

silane concentration with plasma, \( c_{pl} = \frac{p_{SiH_4}}{p_{process}} \)

silane input concentration, \( c = \frac{p_{SiH_4}^0}{p_{process}} \)

\( p_{SiH_4} + p_{H_2} = p_{process} \)

2 parameters, c & D, define the plasma composition
The plasma "black box" becomes a \( \{c, D\} \) unit box.

- **pure silane**
- **ininitely strong plasma**
- **vanishingly weak plasma**
- **infinitely diluted silane**

The diagram illustrates the relationship between silane input concentration, \( c \), and silane depletion fraction, \( D \). The "plasma dimension" is highlighted, showing the transition from vanishingly weak to infinitely strong plasma as silane is depleted.
Contours of constant plasma composition

\[ c_{pl} = c (1 - D) = \text{const.} \]
Contours of constant plasma composition

$c_{pl} = c(1 - D) = 0.05$

- 5% silane, 95% hydrogen
- NO input dilution, 95% depletion

(IN THE PLASMA)

- 5% silane, 95% hydrogen
- strong input dilution, weak depletion

(IN THE PLASMA)
Same plasma composition = same film properties

Constant plasma composition, \( c_{pl} \), gives constant film properties

Depletion is an intensive parameter: same depletion gives same plasma conditions
Microcrystalline silicon can be deposited even with high silane concentration, provided that the silane depletion fraction is sufficiently high, because then the plasma is dominated by hydrogen.
Two regimes of operation

REGIME 1 "conventional": Film crystallinity governed by hydrogen dilution of silane, 'independent' of plasma.

REGIME 2 "recent": Film crystallinity governed by strong plasma depletion, even for high silane concentration.
Simple plasma chemistry model

Based on a reduced set of gas phase reactions...

\[ e + \text{SiH}_4 \xrightarrow{k_1} \text{SiH}_2 + 2\text{H} + e \]

\[ e + \text{H}_2 \xrightarrow{k_H} 2\text{H} + e \]

...and simplified, multi-step, surface reactions.

\[ \text{SiH}_2 \xrightarrow{S} \text{Si}_{\text{surf}} + \text{H}_2 \]

\[ \text{H} + \text{H}_{\text{surf}} \xrightarrow{} \text{H}_2 + \text{vacancy} \]

\[ \text{H} + \text{vacancy} \xrightarrow{} \text{H}_{\text{surf}} + \]

\[ \text{H} \xrightarrow{R} \frac{1}{2}\text{H}_2 \]
Simple, analytical plasma chemistry model

A zero-dimensional model can be appropriate to showerhead reactors (see section I)

"a" is the inverse residence time, an effective "pumping speed"
0-dimensional model; first order reaction rate balance for each species.

\[
\text{SiH}_4 : \ \Phi_{\text{SiH}_4} - (k_{ne} + a)n_{\text{SiH}_4} = 0
\]

\[
\text{SiH}_2 : \ k_{ne}n_{\text{SiH}_4} - S_n_{\text{SiH}_2} = 0
\]

\[
\text{H}_2 : \ \Phi_{\text{H}_2} + \frac{1}{2} R n_{\text{H}} + S n_{\text{SiH}_2} - (k_{Hn_{ne}} + a)n_{\text{H}_2} = 0
\]

\[
\text{H} : \ 2k_{ne} n_{\text{SiH}_4} + 2k_{Hn_{ne}} n_{\text{H}_2} - R n_{\text{H}} = 0
\]

Simple, analytical plasma chemistry model

- Just one silane dissociation channel here: $e + \text{SiH}_4 \rightarrow \text{SiH}_2 + 2\text{H} + e$
- More detailed plasma chemistry only changes the numerical constants:
- ... the general conclusions remain the same.

Hydrogen and silane are the dominant partial pressures; so we can expect radical densities to depend on them.

$$\frac{\Gamma_H}{\Gamma_{\text{SiH}_2}} = \frac{Rn_H}{Sn_{\text{SiH}_2}} = 2 \frac{k_H}{k} \left( \frac{n_{\text{H}_2}}{n_{\text{SiH}_4}} \right) + 2 = 2 \frac{k_H}{k} \left( \frac{1}{c_{\text{pl}}} - 1 \right) + 2$$

"This shows why the plasma deposition is determined by $c_{\text{pl}}$, the silane concentration in the plasma."
Depletion accounts for many of the plasma parameters

\[ D = \left( 1 + \frac{a/kn_e}{(1 + c)} \right)^{-1} \]

- \( a \) [s\(^{-1}\)] = inverse residence time = effective pumping speed = \( 6.1 \times 10^{-6} \frac{T_{\text{gas}} \Phi_{\text{total}}}{p \cdot \text{gap} \cdot \text{area}} \);
- \( kn_e \) [s\(^{-1}\)] = silane dissociation rate = plasma dissociation frequency = \( F(P_{RF}, f [\text{MHz}]) \);
- \( c \) = silane input concentration, \( \frac{\Phi_{\text{SiH}_4}}{\Phi_{\text{total}}} \).

Depletion scaling:

- \( D \uparrow \) if any of \( \{p, \text{gap}, \text{area}, c, P_{RF}, f\} \uparrow \) &/or \( \{\Phi_{\text{total}}, T_{\text{gas}}\} \downarrow \)
Intermediate Conclusions

• Plasma composition and deposition depend on the silane concentration in the plasma, \( c_{pl} = c(1-D) \), and not only on the silane concentration in the input flow, \( c \).

Strong hydrogen dilution in the plasma, and \( \mu c \)-Si:H deposition, can be obtained with high input concentration of silane and strong depletion.

• The fractional depletion of silane, \( D \), is an intensive parameter.

Depletion measurement could be a useful diagnostic check for the same plasma conditions in the transfer of process parameters to an upscaled reactor. Monitored non-intrusively by infrared absorption spectroscopy in the pumping line.

• A zero-dimensional model, appropriate for a uniform large-area reactor, can be used to estimate the relation between intensive plasma parameters.