Evaluation of ESH Impact for Plasma Etch: Etch By-Products

Matthew Radtke, Mark Nierode, J.W. Coburn, Dave Fraser and David B. Graves

Department of Chemical Engineering, University of California, Berkeley

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Summary of Goals for Plasma Etch*

Characterize and minimize ESH impact of etch and chamber clean by-products and emissions, especially PFC’s.

Develop plasma modeling and simulation methods to extend, generalize and integrate advances into a systems-level ESH/process development optimization.

Reduce plasma equipment energy use.

* ITRS: ESH, FEP and Interconnect Chapters
Challenge for Semiconductor Industry: Continued Scaling

- New device structures and new materials will be introduced into manufacturing over the next decade to achieve scaling goals.
- Challenges in manufacturing will be in simultaneously optimizing for process objectives and ESH objectives.
- Plasma etch appears to offer special challenges for several reasons:
  - plasma creates new materials: etch by-products
  - often observe by-product re-deposition on walls/wafer
  - plasma is unusually complex chemical environment complicating control strategies
New Materials: High and Low $\kappa$ Dielectrics*

- ZrO$_2$, HfO$_2$, BST, TaO$_5$, Y$_2$O$_3$, (Zr, Hf, Ti,...)SiO$_4$, ...
- SILK, organic polymers, polymer-SiO$_2$ composite, porous materials

*ITRS FEP and Interconnect Chapters
Metal Gate Electrode Materials*

Required properties:
- Appropriate work function
- High $T_m (>1000^\circ C)$
- Stable interface with gate dielectric
- Compatible with Si processing – deposition, etch

Candidate materials:
- High-$T_m$ metals (Ta, Mo, Ru, W)
- Metal nitrides (MoN, WN, TiN)
- Doped metal oxides (In$_2$O$_3$, SnO$_2$, RuO$_2$)
- Metal silicides (CrSi, WSi$_x$)

* T.J. King, ERC Retreat, 2001
Typical Etch Gases

- \( \text{Cl}_2, \text{HCl}, \text{Br}_2, \text{HBr} \ldots \)
- \( \text{O}_2, \text{N}_2, \text{H}_2 \ldots \)
- \( \text{CF}_4, \text{HCF}_3, \text{C}_2\text{F}_6, \text{C}_4\text{F}_8, \text{SF}_6, \text{NF}_3, \ldots \) (PFC’s & HFC’s)
- \( \text{CH}_4, \text{C}_2\text{H}_6, \ldots \)
Many Possible New Materials/Etch Gases

- Clear need for a systematic approach
- Need methods to identify potential ESH-sensitive compounds formed during etch/clean
- Need methods to model or predict compound formation to minimize costs of examining all alternatives
- Need ways to combine process and ESH objectives optimization
Simultaneous Process and ESH Objective Optimization

- Etch by-products play central role in both process effects and ESH concerns
- Critical dimension and selectivity control in etch strongly affected by deposition or re-deposition of etch products and/or etch gas decomposition products
- Etch/chamber clean emissions control center around gas phase/wall species
- Project *naturally combines process and ESH goals*
Etch Chamber with No Plasma

Etch Gases Flowing In

Chamber walls:
- SiO₂
- Al₂O₃
- Si
- Si₃N₄

SiO₂

Photoresist

Chamber Effluent Flowing Out:
Inlet Gases
Etch Chamber with Plasma On

Plasma creates all possible combinations of inlet gas, film, and chamber wall materials.

Etch Gases Flowing In:
- CF$_4$
- C$_2$F$_6$
- C$_4$F$_8$
- CHF$_3$
- Ar
- He
- O$_2$
- N$_2$

Etch products on chamber walls:

Chamber walls:
- SiO$_2$
- Al$_2$O$_3$
- Si
- Si$_3$N$_4$

Chamber Effluent Flowing Out:
Etch Chamber with Plasma On: Chamber Wall Cleaning

Clean Gases Flowing In
Ar
SF₆
O₂

New set of chemistries during chamber clean

Etch products on chamber walls

Chamber Effluent Flowing Out

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Downstream Plasma: POU Plasma Abatement in Foreline

- Chamber Effluent Flowing Out
- POU Plasma for PFC Abatement
- To Dry Pump and Stripping
- H₂O

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Experimental Apparatus

FTIR in turbo pump foreline
Etch Chamber (side view)

- Gas inlet
- 5-turn coil and Faraday shield
- Quartz Crystal Microbalance
  - etch rate measurement
  - rf biased
  - loadlock
- ICP
- Etch Byproducts
- Chuck
  - release etch byproducts into plasma
  - shielded
  - rf biased
- Pump

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Preliminary Experimental Results: Si/Cl₂/O₂

• Si etch to establish base case for comparison to proposed metal gate electrode materials
• What happens to etch products?
  – What fraction of etch products ionize?
  – What fraction of positive ions contain etch products?
• Important question to address is extent of etch product re-deposition on chamber walls (and therefore on wafer)
Strategy

- Study system in which we know etch product re-deposition occurs: Si etching w/ O₂/Cl₂
- Measure wall deposition rates and corresponding ion and neutral fluxes to establish re-deposition mechanism.

Experimental Conditions

Pressure: 3, 10 mT
Substrate Bias: 0, -50, -100V
Coil Power (deposited): 150 W
Inlet Gas Composition: Cl₂ & O₂ : 0, 5,10, 20% O₂
  (3mT ~ 8 sccm, 10mT ~ 20 sccm)
*1-2 sccm of He backside wafer cooling
SiOCl Wall Deposition Rates

- maximum deposition rate with bias (wafer etching) and O₂ added
Ion Flux to Walls

- Ion composition ranged from 0-63% silicon-containing
- Absolute ion fluxes calibrated from ion probe

3 mT, 10% O₂
100V bias

% Ion Flux

AMU

0 5 10 15 20 25 30 35 40 45 50

20 40 60 80 100 120 140 160

Si⁺ Cl⁺ Cl₂⁺ SiCl⁺ SiCl₂⁺ SiCl₃⁺ SiCl₄⁺ O⁺ SiO⁺ ClO⁺ SiOCl⁺
APMS on SiCl\textsubscript{x} Neutral Species

- SiCl and SiCl\textsubscript{2} are dominant SiCl\textsubscript{x} radicals
- no SiCl\textsubscript{3} observed at experimental conditions (trace SiClO observed)
Deposition Rate vs. Incident Flux (10 mTorr)

- $R_{\text{growth}} \propto \Gamma_{\text{SiCl}_x^+}$
- $\Gamma_0 >> \Gamma_{\text{SiCl}_x}$
- Absolute radical fluxes estimated from radical direct ionization cross sections
Deposition Rate vs. Incident Flux (3 mTorr)

Inlet: 10% O₂

- \( \Gamma_{\text{SiCl}_x^+} ; \Gamma_o \gg \Gamma_{\text{SiCl}_x^+} \); ion mass flux can account for wall mass increase

Inlet: 20% O₂

Major conclusion: SiOCl wall deposition strongly correlates with surface flux of Si-containing positive ions
Similar Studies for Other Materials: e.g. Metal Gate Electrode Etch

- New metal gate materials may create various unknown toxic/hazardous by-products during etching

- Similarly to Si, these materials are likely to ionize readily in plasma (metals generally have low ionization potentials)

- Look for correlation between etch-product-containing ions and wall re-deposition

- Examine wall deposit composition

- Look for neutral volatile species that might pose ESH risk
RuO₂ Etching in O₂-Containing Plasma

- Ru, RuO₂ are potential metal gate electrode materials for use with high k gate dielectrics
- Do etch by-products contain RuO₄? Is it formed in plasma?
- RuO₄ major concern for toxicity: minimize formation/emission
Plasma Composition: Ions

- 0-2% of ions contained Ru
- Significant Ru etched w/out bias
* Temperature dependent

**AMU**

0 20 40 60 80 100 120 140 160

% of Total Ions

% RuO\text{x}^+

Bias (V)

3 mTorr

10 mTorr

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Plasma Composition: Neutrals

- trace amounts of Ru (372.8nm) observed with OES
- APMS detected trace amount of Ru; no RuO_x neutrals detected
- neutral Ru species may be nearly completely ionized: low ionization potentials (Ru: 7.37eV)
- Deposition rate proportional to RuO$_x^+$ ion mass flux to surface
- Ion mass flux to wall $\sim$ 3-4X greater than deposition rate, implying some deposited Ru is re-etched or ion sticking probability not unity
Concluding Remarks

1. Etch product ionization followed by wall deposition appears to be a dominant mechanism for etch product transport in many etch chemistries. (Evidence in ZrO$_2$ etch for Zr-wall deposition presented by Jim McVittie and co-workers at Stanford).

2. This limits flow of potentially toxic/hazardous materials to foreline and fab exhaust systems, e.g. RuO$_4$ appears not to leave chamber in detectable quantities during RuO$_2$ etch.

3. However, wall deposits pose potential risks to operators.

4. Chamber wall cleaning must also be studied: wall-deposited etch product removal important for tool effectiveness, energy and consumables, as well as potential ESH impact.
5. Wall deposit composition needs to be measured.
6. Many more materials must be studied.
8. Development of etch by-product models under development, continuing the work of former ERC student Mark Kiehlbaugh (Lam Research).
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