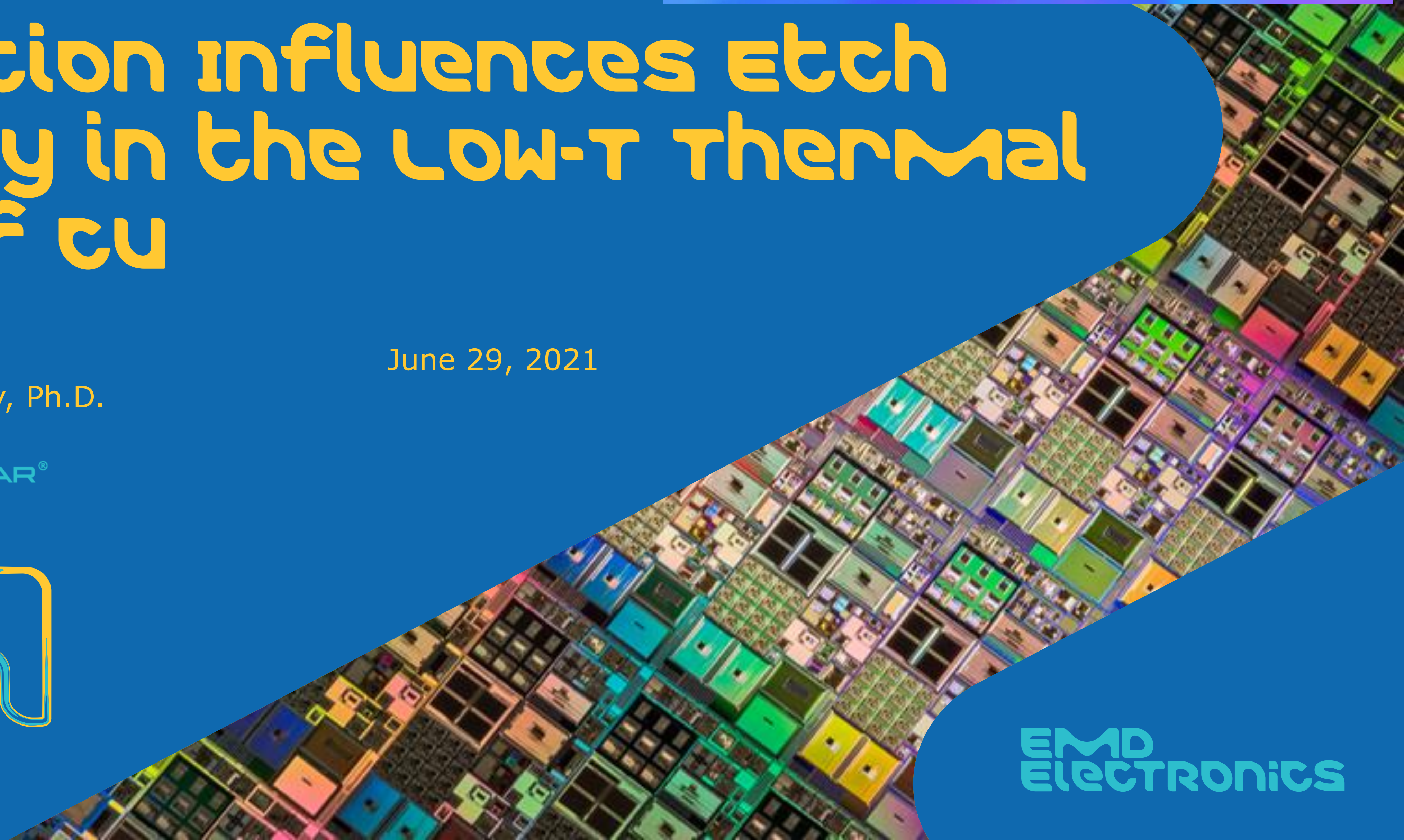
ALD 2021
21st International Conference on Atomic Layer Deposition
JUNE 27-30, 2021 • VIRTUAL MEETING
ATOMIC LAYER ETCHING
Featuring the 8th International Atomic Layer Etching WORKSHOP

# Oxidation influences etch quality in the low-T thermal ALE of Cu

**LI-ALE-TuM3-24**
Martin E. McBriarty, Ph.D.

June 29, 2021

INTERMOLECULAR®

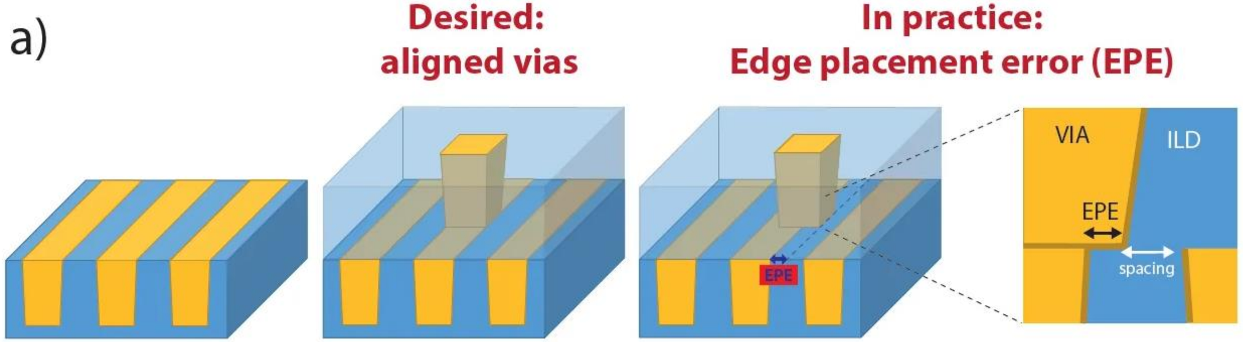


EMD ELECTRONICS

# Metal Recess Etch in Semiconductor Applications
## Fully Self-Aligned Vias (FSAV)

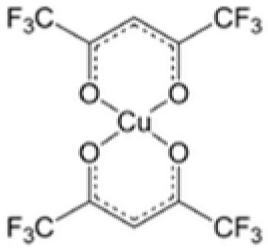
Impending issue in scaling down back-end-of-line (BEOL) metal patterning:

- Lateral displacement of vias due to mask alignment error → **shortened spacing** between vias & neighboring lines
  - **RC delay** and **early device failure**
- Solution: **FSAV scheme**, where spacing is increased by *either*:
  - Dielectric buildup with area-selective deposition (ASD) → *requires etch of stray nucleation*
  - Metal recess by atomic layer etch (ALE)



**FSAV scheme using metal recess etch**
https://**www.atomiclimits.com**/2019/07/18/fully-self-aligned-vias-the-killer-application-for-area-selective-ald-a-discussion-of-the-requirements-for-implementation-in-high-volume-manufacturing/

# BEOL Metal ALE Using Beta-Diketones
## Surface Modification & Hhfac Volatilization



**Cu ALE by oxidation/Hhfac**

$O_3$ oxidizes $Cu^0$ to $Cu^{2+}$ (CuO) [room T + UV]:

$$CuO + 2Hhfac \rightarrow Cu(hfac)_2 + H_2O$$

$O_2$ oxidizes $Cu^0$ to $Cu^{1+}$ ($Cu_2O$) [275 °C]:

$$Cu_2O + 2Hhfac \rightarrow Cu(hfac)_2 + Cu + H_2O$$

- $Cu^{1+} \rightarrow Cu^0 + Cu^{2+}$ disproportionation → unique physico-chemical complexity

Mohimi, Abelson *et al.*, *ECS JSST* **7** (2018) P491

**Co ALE by $Cl_2$/Hhfac**

$Cl_2$ oxidizes $Co^0$ to $Co^{2+/3+}$ [140 °C]:

$$CoCl_x + xHhfac \rightarrow Co(hfac)_x + xHCl$$

- AFM shows dramatic surface smoothing (5.3nm → 0.7nm)
- *In situ* XPS shows hfac decomposition byproducts → F, C, O remain on surface

Wang and Opila, *JVSTA* **38** (2020) 022611

# Cu ALE by oxidation / Hhfac

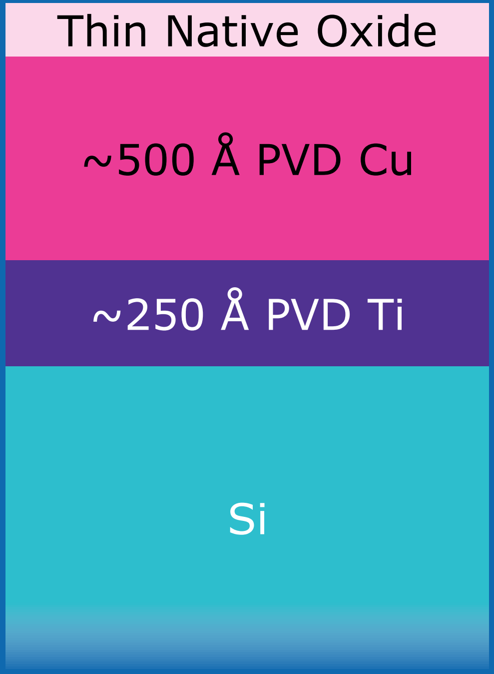
## Process Summary

- **Intermolecular A-30**
  - 300mm ALD Tool
  - 44mm coupons on a 300mm carrier wafer
- **Cycle (50x – 300x):**
  - Dose Hhfac (1s)
  - Purge with Ar (45s)
  - Dose reactant (0.5 – 30s)
  - [$O_2$, 20% $O_3$ bal. $O_2$, or $H_2O$]
  - Purge with Ar (30s)
- **Process pressure: 2 Torr**
- **Sample temperature range: 150 – 250 °C**

## Metrology

XRF, XPS, AFM

## Sample Stack



Thin Native Oxide

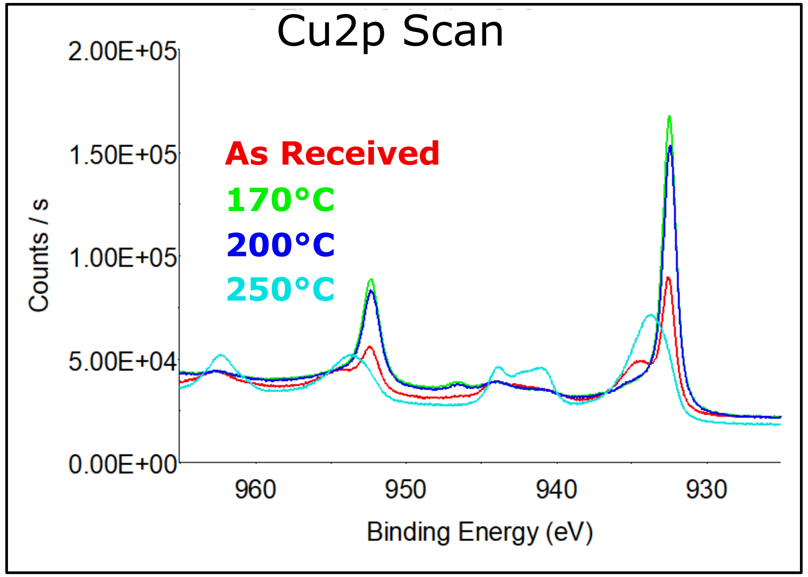
~500 Å PVD Cu

~250 Å PVD Ti

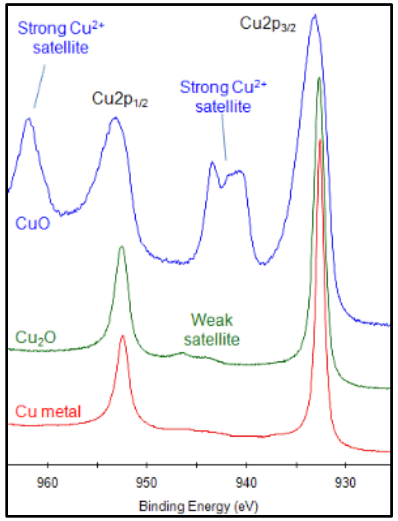
Si

# Cu ALE by Oxidation / Hhfac
## **Initial Surface Characterization (XPS)**

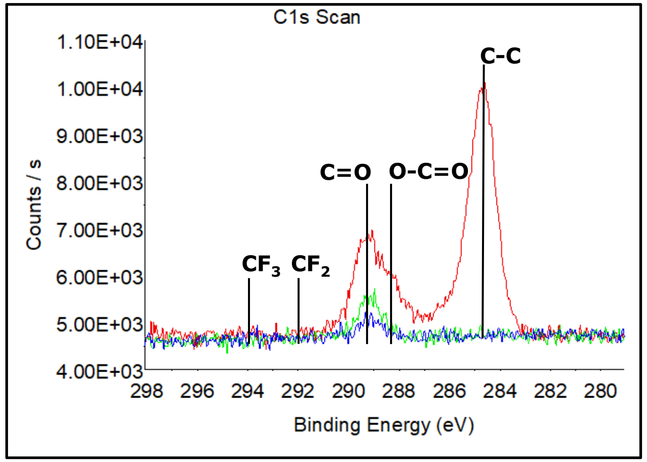
- As-received, surface Cu state is $Cu^{1+}$
  - Native oxide is a combination of $Cu^{1+}$ oxide, hydroxide, and carbonate
- 60s $O_2$ at 170 – 200 °C removes Cu hydroxyl & carbonate but maintains $Cu^{1+}$ oxidation state
- 60s $O_2$ at 250 °C in $O_2$ yields surface $Cu^{2+}$

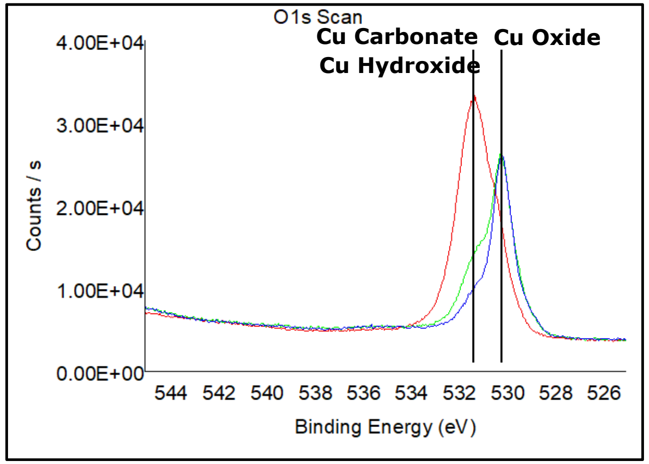


### *Peak Reference*



www.xpssimplified.com



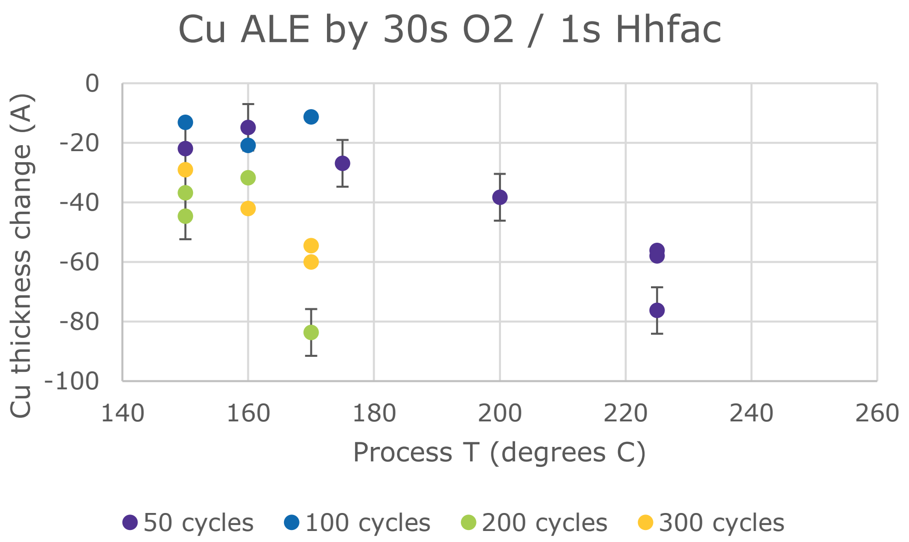


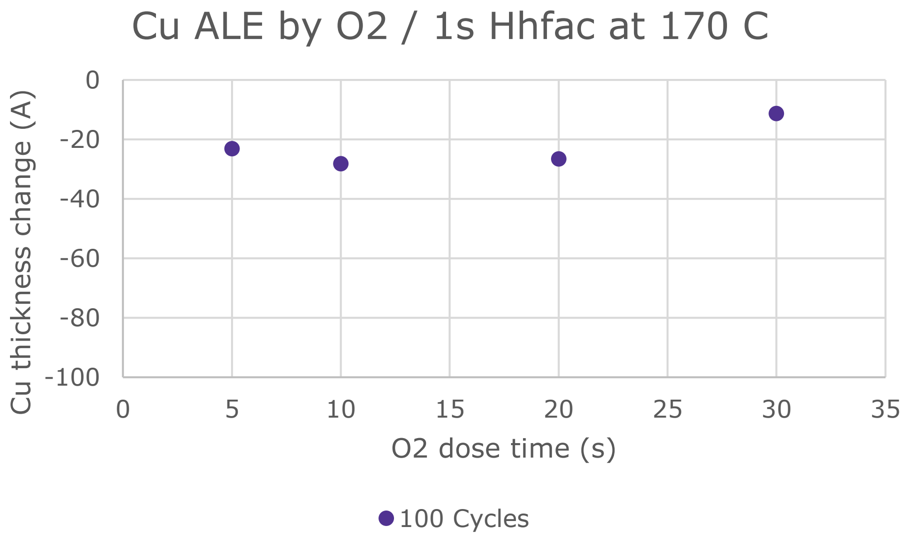
**As Received**
**$Ar^+$ Sputter 1**
**$Ar^+$ Sputter 2**

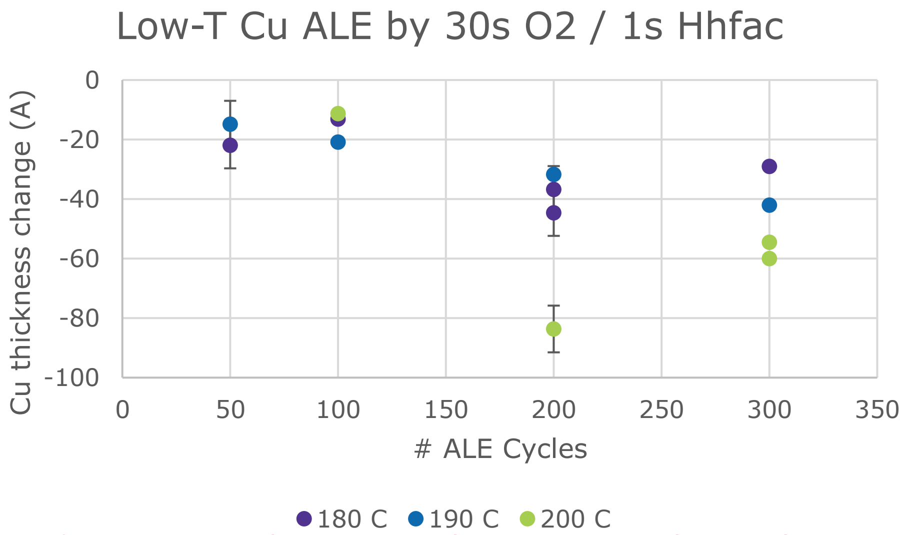
# Cu ALE by Oxidation / Hhfac

# $O_2$ / Hhfac Process Trends

- Increasing etch with increasing temperature
- Inconsistent etch at low temperatures / low cycle counts



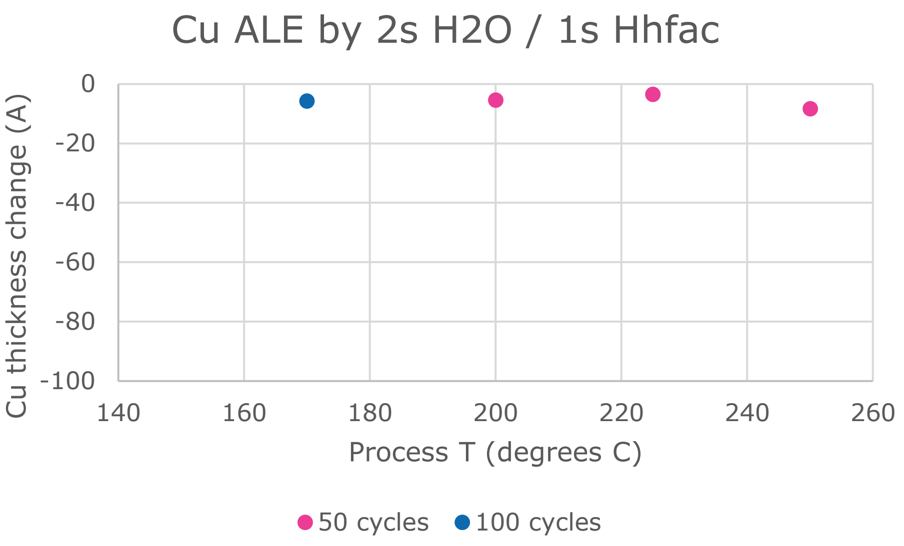


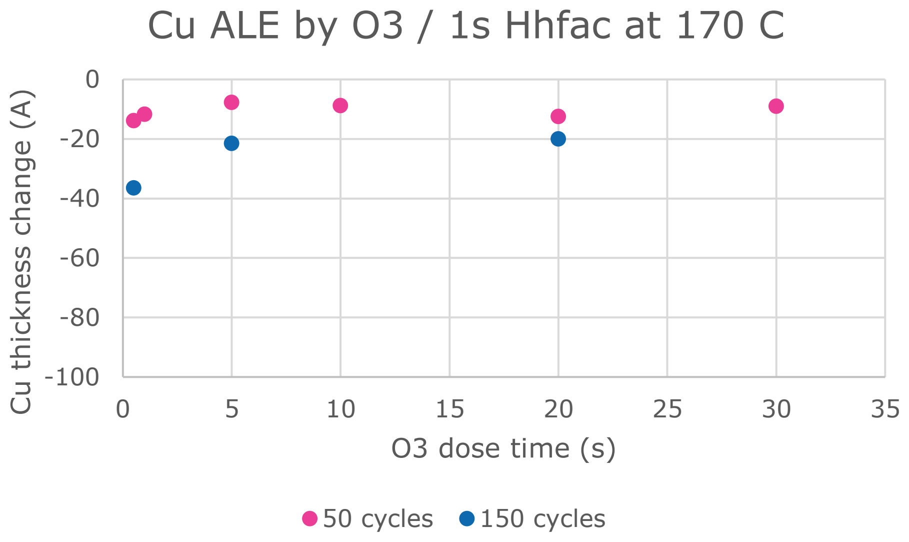


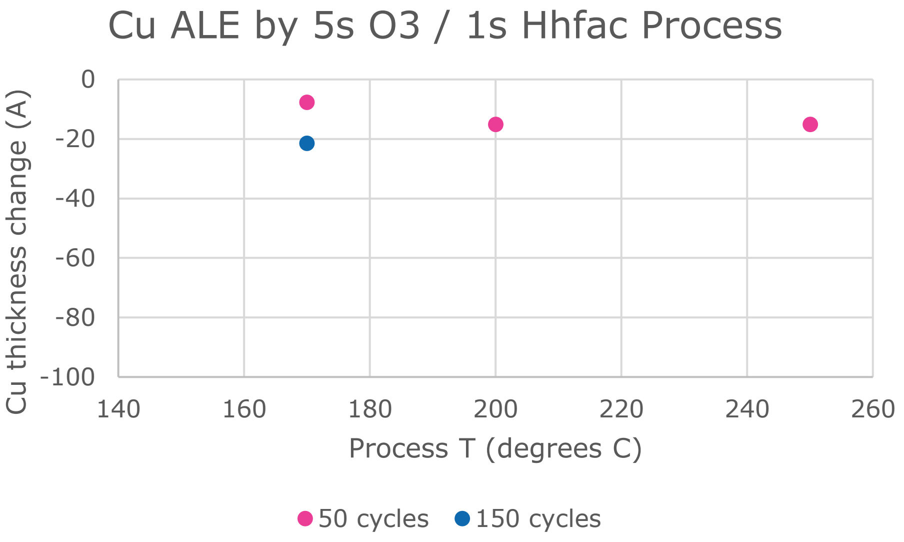
**Uncertainties due to incomplete XRF protocols in early experiments*

# Cu ALE by Oxidation / Hhfac
# **Effect of Alternate Oxidizers**

- $H_2O$: Minimal etch, no clear etch trend
  - No improvement in etch if $H_2O$ dose is increased (not shown)
- $O_3$: More etch than $H_2O$, but less etch than $O_2$
  - Greater etch with *shorter* $O_3$ dose time



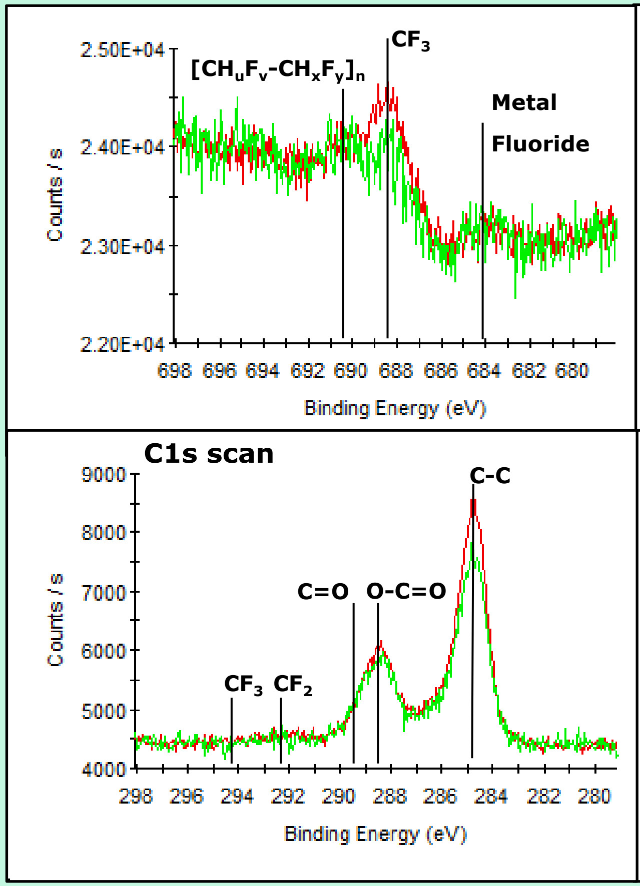




# ALE of Cu: **Process Insight by Surface Analysis**

**No Sputter**
**Gently Ar$^+$ Sputtered**

### 150 °C O$_2$ / HFAC

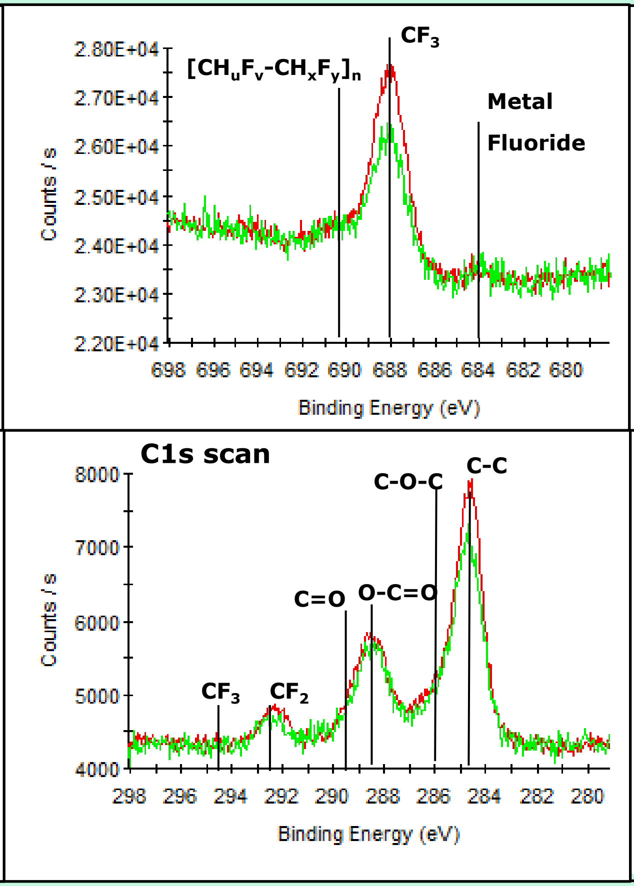


**200 cycles**

**29 – 52 Å Cu Removed**

**AFM Roughness = 0.9 nm**

### 170 °C O$_2$ / HFAC

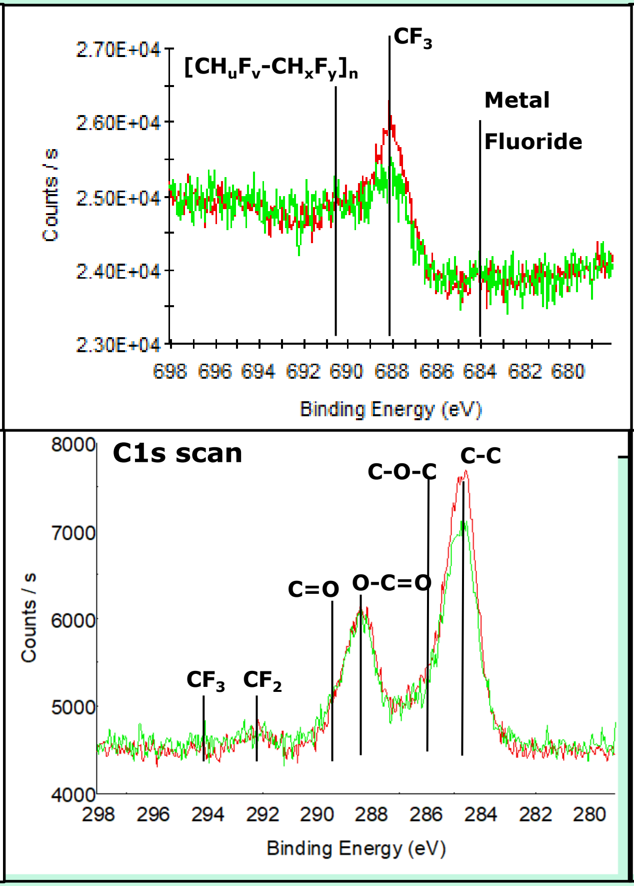


**200 cycles**

**76 – 91 Å Cu Removed**

**AFM Roughness = 2.6 nm**

### 200 °C O$_2$ / HFAC

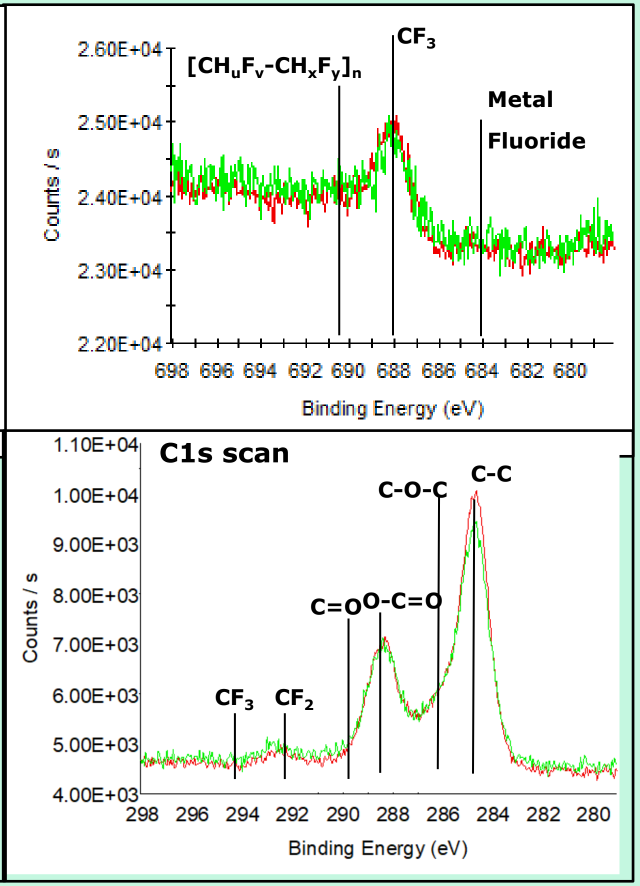


**50 cycles**

**30 – 46 Å Cu Removed**

**AFM Roughness = 2.8 nm**

### 250 °C O$_2$ / HFAC



**50 cycles**

**56 – 84 Å Cu Removed**

**AFM Roughness = 9.0 nm**

Additional XPS analysis (not shown):

**Post-etch surface Cu is largely Cu$^{1+}$**

# Conclusions

# Cu ALE by Oxidation / Hhfac

## Process Robustness and Reproducibility

- Variability obscures process trends
- No clear "ALE window"
- High cycle counts (≥200) required for significant etch at lower temperatures

## Surface Quality

- Over-oxidation appears to *slow* ALE process
  - Surface effect or chamber effect?
- hfac residues (C, O, F) are undesirable for HVM integration
  - Residues could also block etch reactions

## Other Caveats

- Oxidized Cu may be "invisible" to resistance and XRR analysis, falsely indicating etch
  - Resistance measurement is sensitive to **metallic Cu**
  - XRR may be insensitive to low-density surface oxides
  - The most reliable metrologies should be **directly sensitive to all Cu**, e.g. XRF

# Conclusions

## ALE Process Design with the Application in Focus

For fully self-aligned vias, the ALE process **must:**

- Be effective within BEOL thermal budget constraints
- Have robust process windows
- Not leave residues that could affect device performance OR downstream processes
- Use safe chemistries that can be made available in bulk

Proposed focuses of ALE research beyond epc:

- Surface quality
  - Condition of starting surface
  - Contamination / oxidation
- Device performance
  - Test vehicles (e.g. model BEOL patterns)
- Selectivity
  - Which materials should *not* be etched?
  - Which materials *could* or *should* be etched, in addition to the target material?
- Chamber conditioning & history
  - How might ALE reactants interact with chamber lines and sidewalls?

**Martin E. McBriarty, PhD** (he/him)
Sr. Scientist

martin.mcbriarty@emdgroup.com
+1 (408) 483-4726
3011 North First St.
San Jose, CA 95134 USA

INTERMOLECULAR®