

Cleaning of Photoresist and Etch Residue from Dielectrics using Supercritical CO₂

Gunilla B. Jacobson,

**Ben Palmer, Deborah Yellowaga, Marie Lowe
Richard Brown, Dirk Dreissig, Max Biberger**

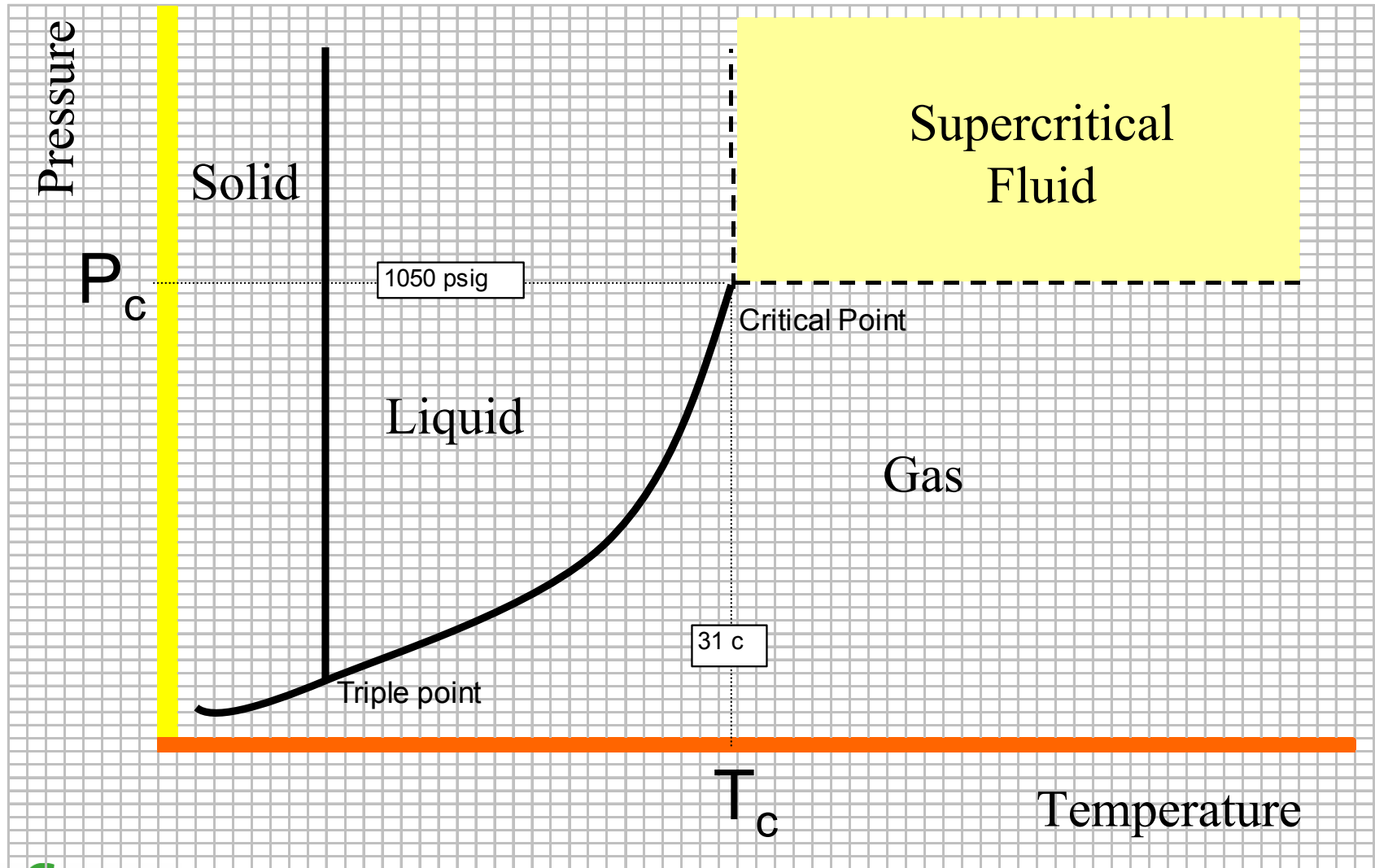
Supercritical Systems Inc.
2120 W. Guadalupe Rd.
Gilbert AZ, 85233



Outline

- Introduction
 - Supercritical Fluids
 - Industrial Applications
- Process Flows
- Hardware and Process Conditions
- Results
- Tools and CO₂ Supply
- Summary

P/T Phase Diagram



Critical Parameters

Fluid	T _c (°C)	P _c (bar)
Xe	17	58
CO ₂	31	73
C ₃ H ₈	97	42
NH ₃	132	113
MeOH	239	81
H ₂ O	374	220

Carbon Dioxide

- Non-toxic, Non-flammable
- Compatible with existing HP equipment
- Inexpensive
- Environmentally friendly

Solvent	Viscosity	Surface Tension	Density
Liquid CO ₂	0.08	1.5	0.87 ³
SC-CO ₂	0.03 ²	≈ 0	0.3 ² -0.8
H ₂ O	1.00	72	1.0

¹at 20° C and 105 atm

²at 35° C and 75 atm

Industrial Applications

- Supercritical Fluid Chromatography
- Supercritical Fluid Extraction
- Synthesis of polymers and pharmaceuticals
- Particle formation
- Degreasing of machined parts
- Dry cleaning of clothing

Semiconductor Applications

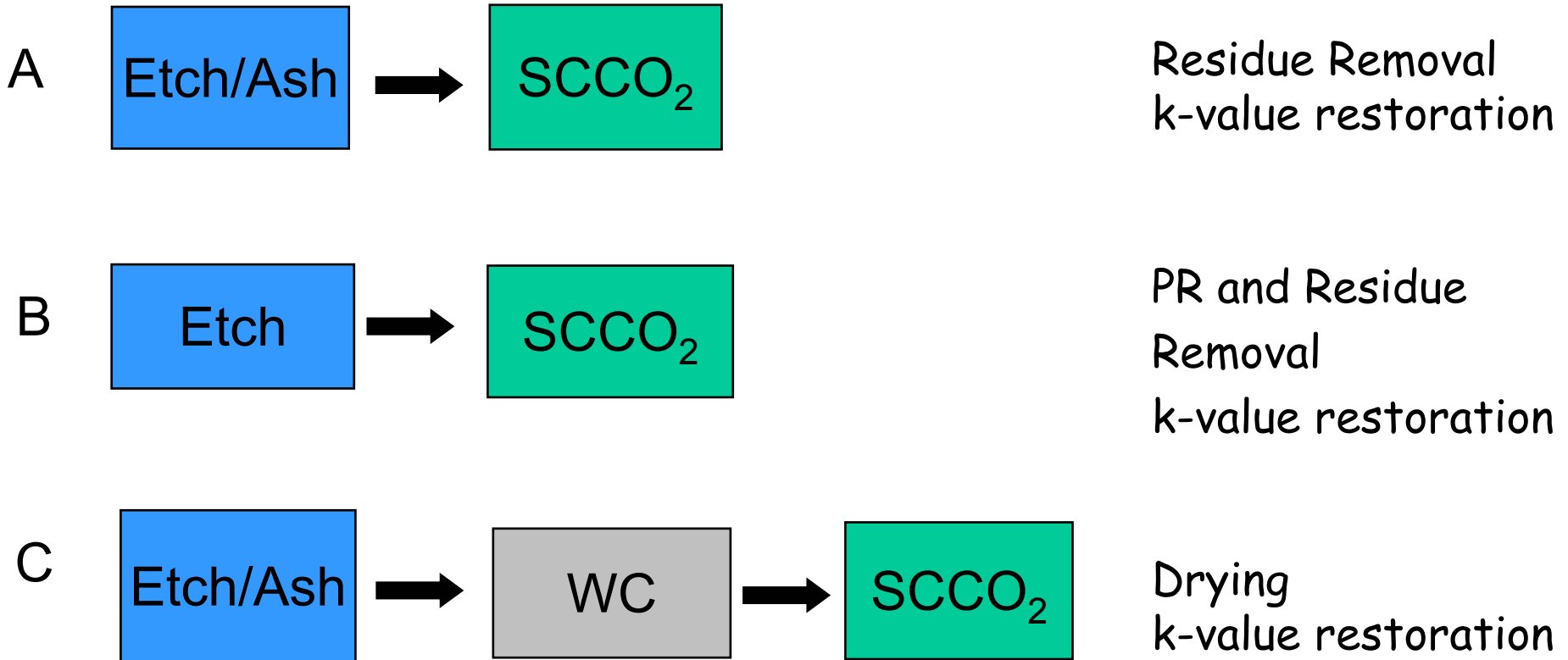
- Post-etch removal of Photoresist and Etch Residue
 - Post dielectric etch
 - Post metal etch
- Post-ash residue removal
- FEOL Cleaning
- k-value restoration
- Via poisoning
- MEMS Technologies
- Post CMP Cleaning

Advantages of SCCO₂

- Yield enhancement for sub 90 nm features
- Virtually no surface tension
 - can clean < 0.1 um CD
 - penetrates into the porous material
- Drying effect, extracts H₂O and organics
- “Dry in - dry out” process
 - leaves no residual solvent
- Compatible with porous low-k and Cu

Process Flows

Benefits

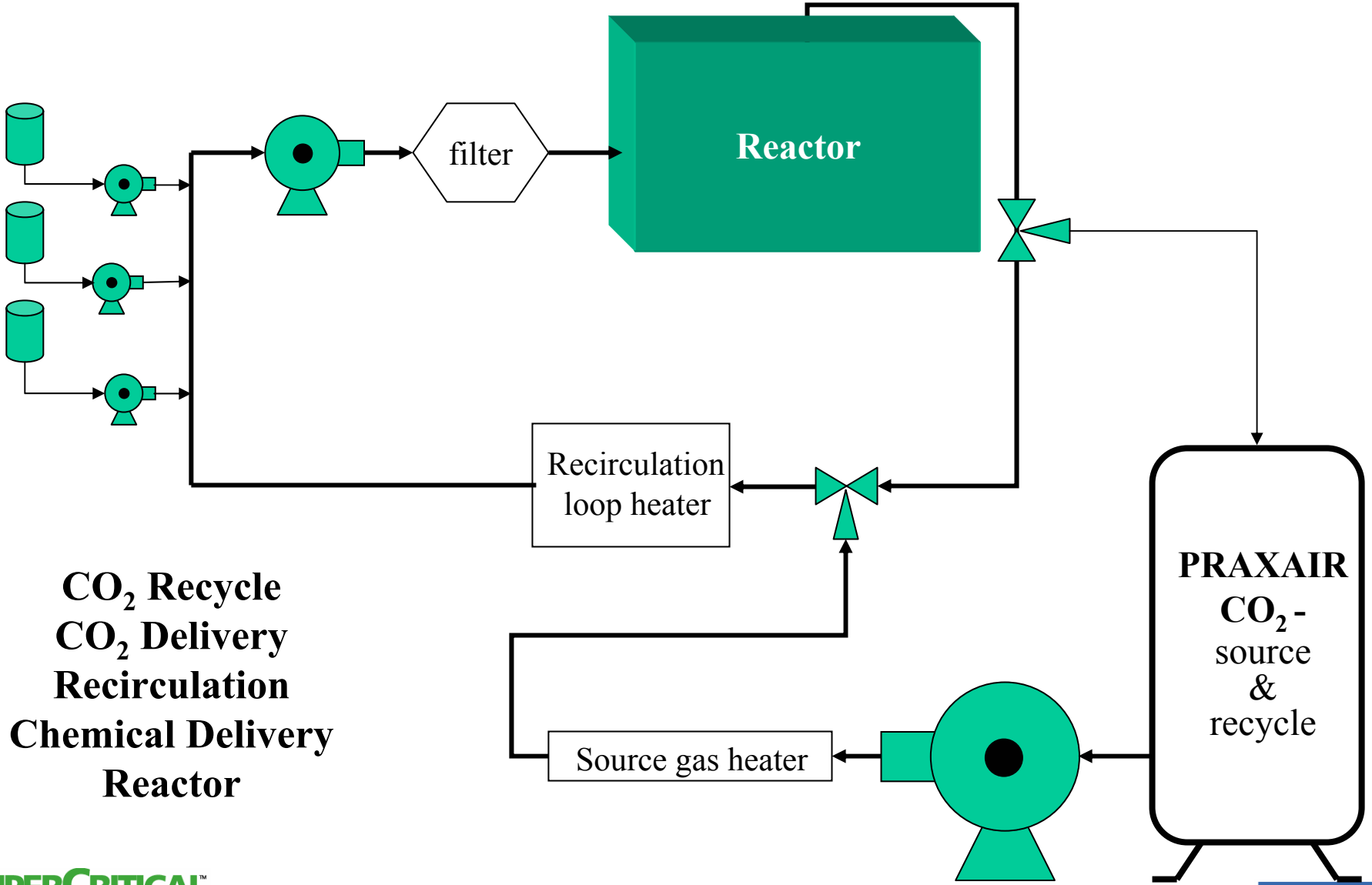


SSI Tools

- Process Development Lab
 - Bench Top Tools
 - Process development on wafer chips

- Process Integration Lab
 - α Tools
 - β Tools
 - Whole wafers runs
 - 200 & 300 mm option on all tools

Hardware



CO₂ Recycle
CO₂ Delivery
Recirculation
Chemical Delivery
Reactor



Process Conditions

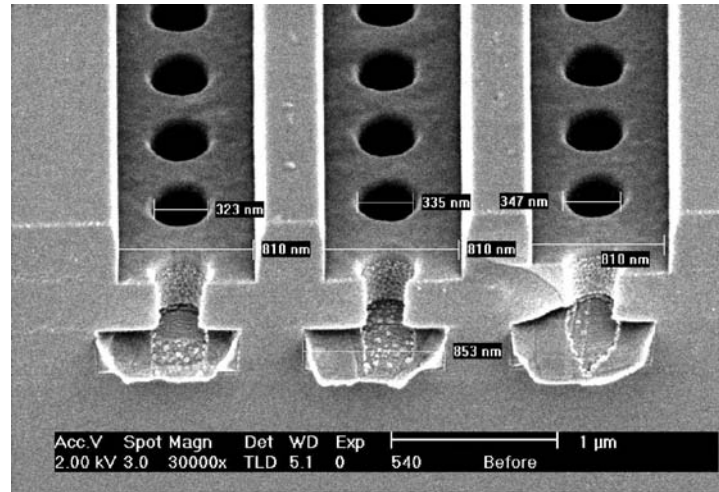
- Typical process conditions:
 - $T = 40-80\text{ }^{\circ}\text{C}$
 - $P = <3000\text{ psi}$
 - Co-solvents: $< 20\text{ ml/wafer}$

Results

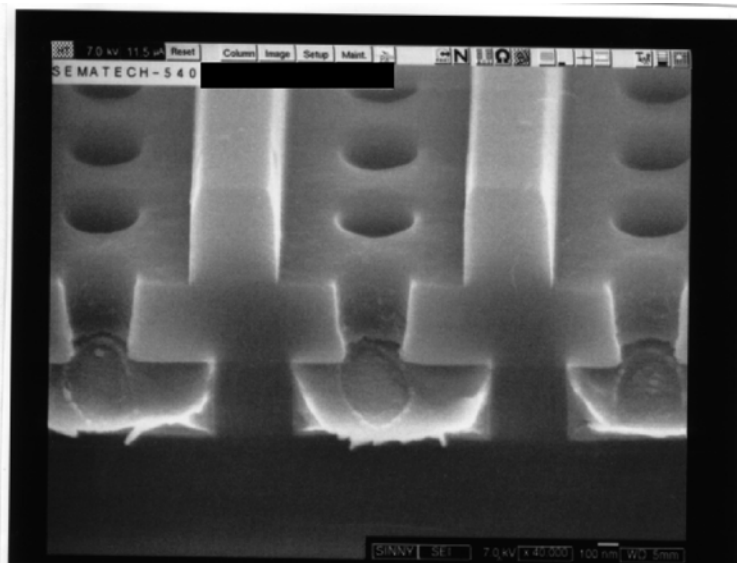
(Post dielectric ash residue removal)

Sematech – 540 (On Chips)

PRE

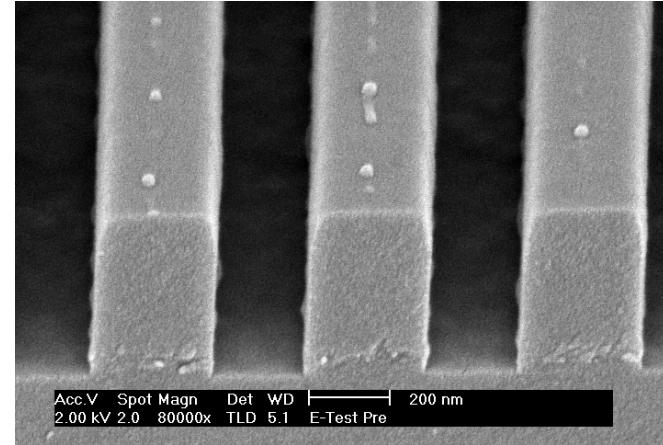
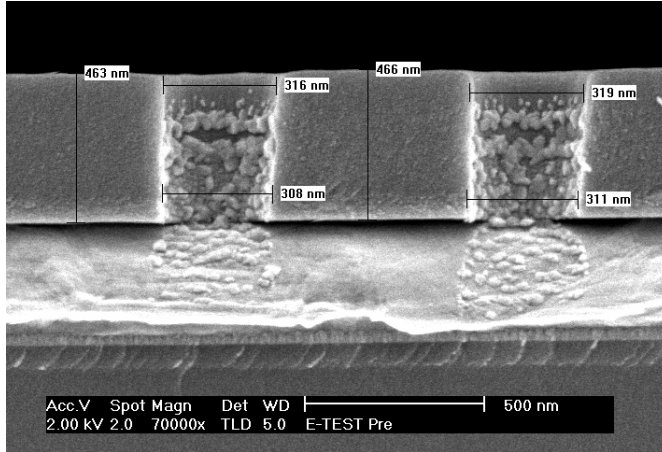


POST

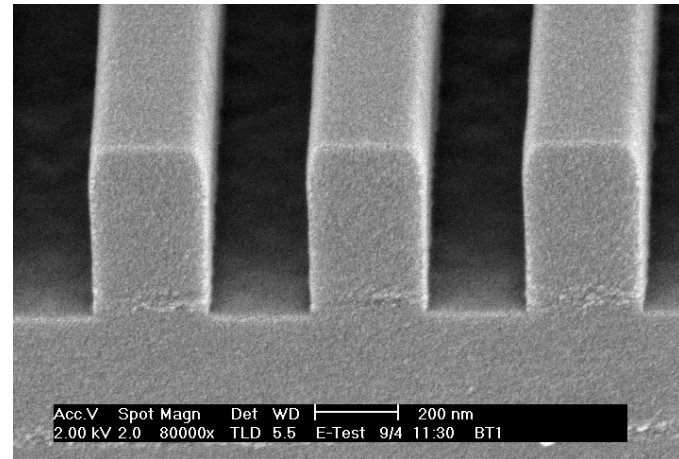
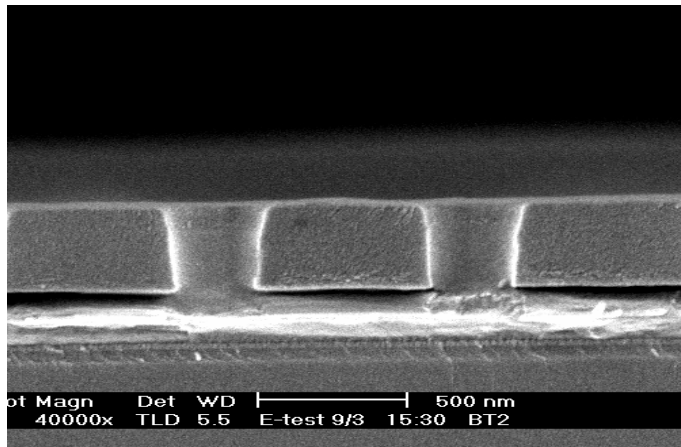


DD JSR Cu Wafers (On Chips)

Pre

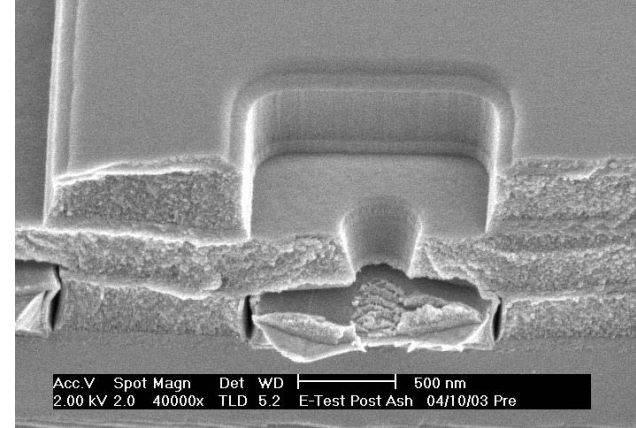
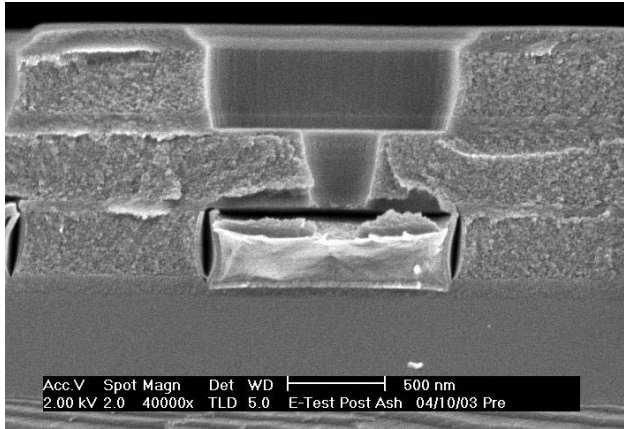


Post

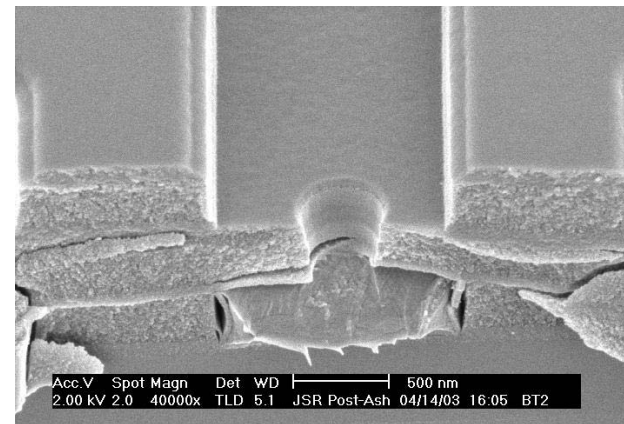
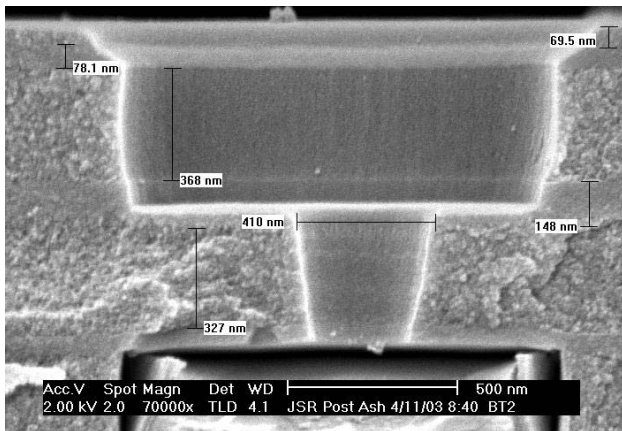


DD JSR Cu Wafers (On Chips)

Pre



Post

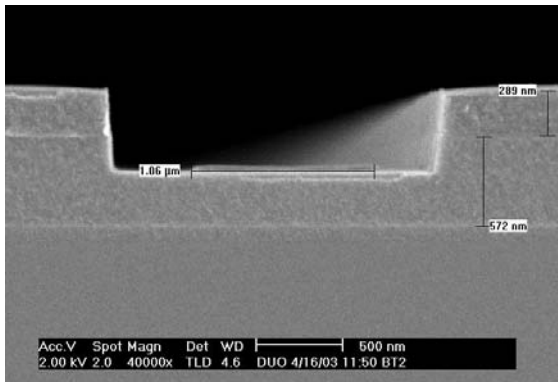
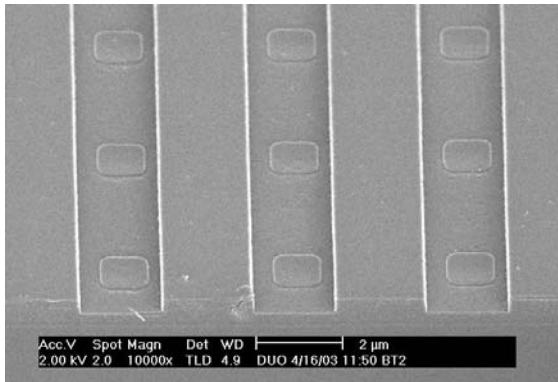


Results

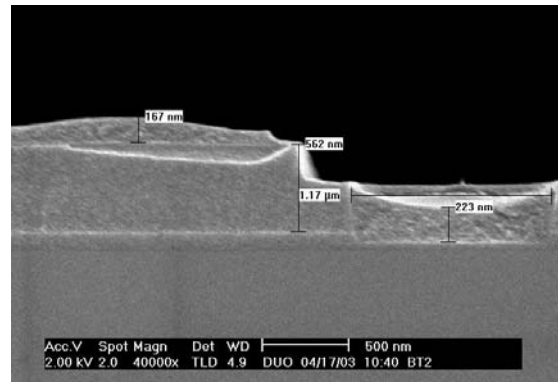
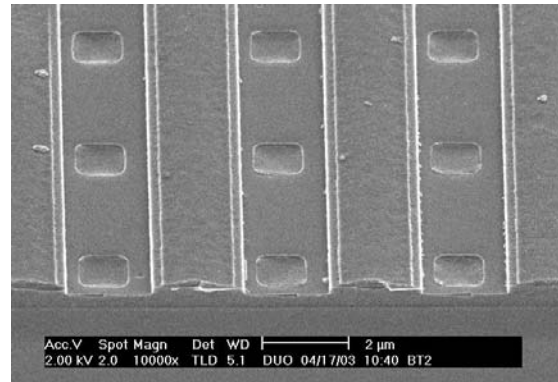
(Post dielectric etch clean)

DUO Removal (On Chips)

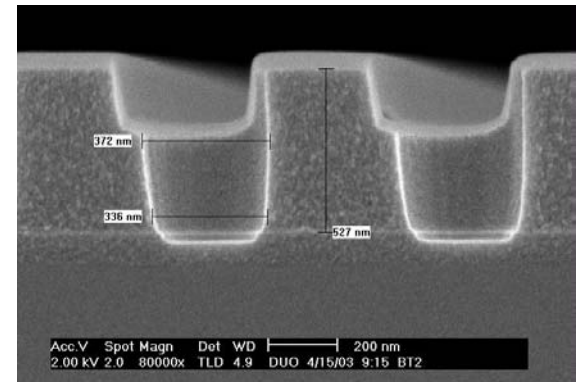
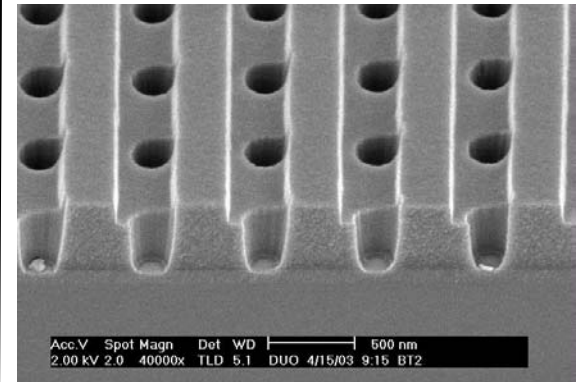
Pre



Post 1/2 BKM

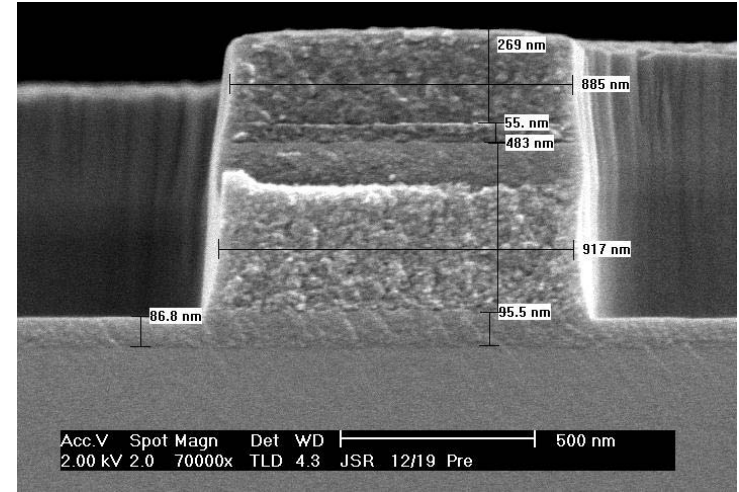
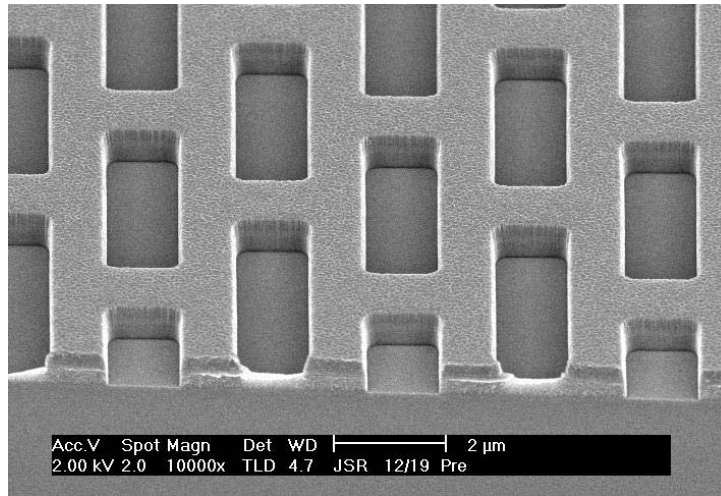


Post BKM

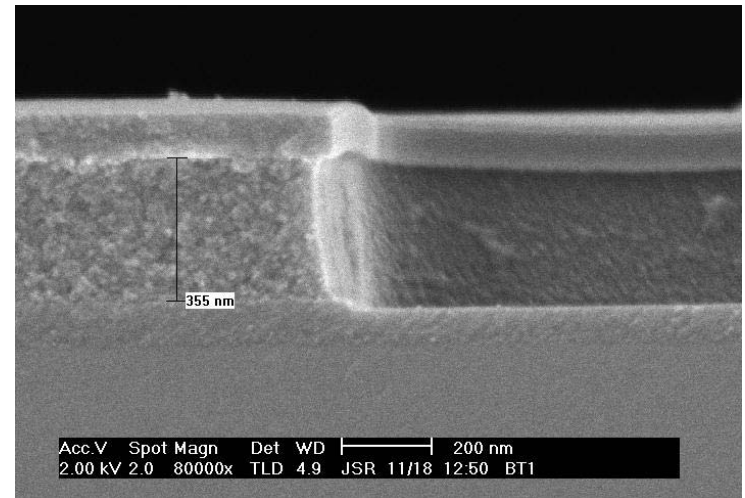
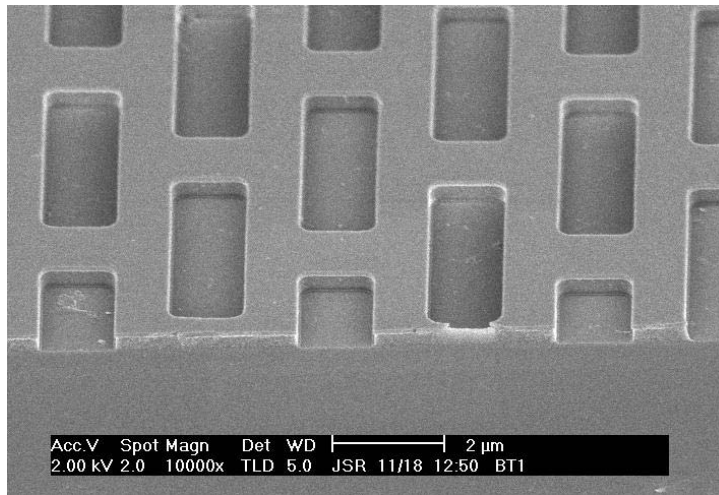


Sematech – JSR (On Chips)

PRE



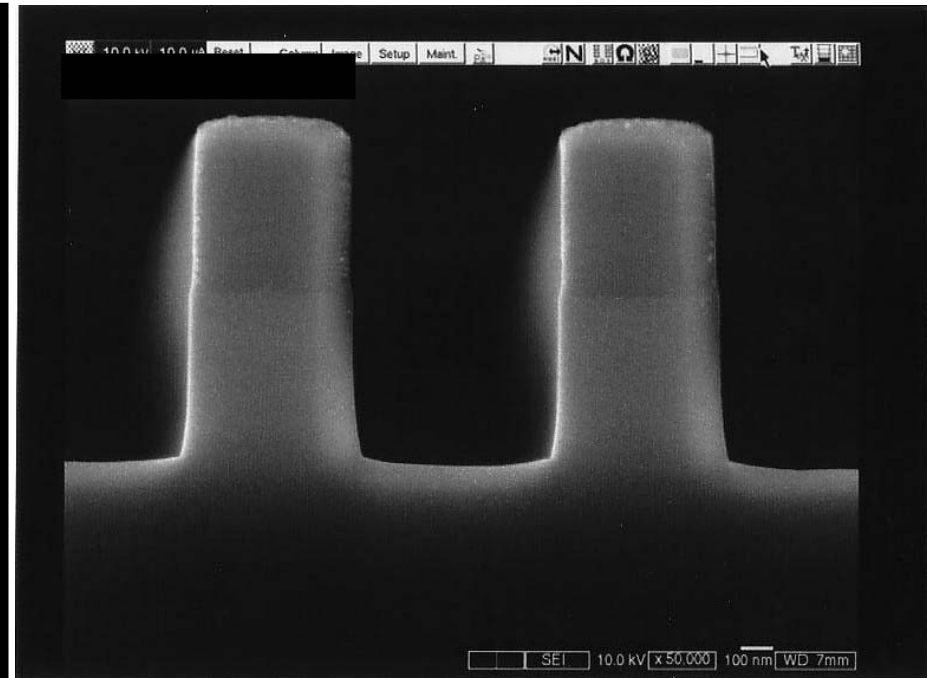
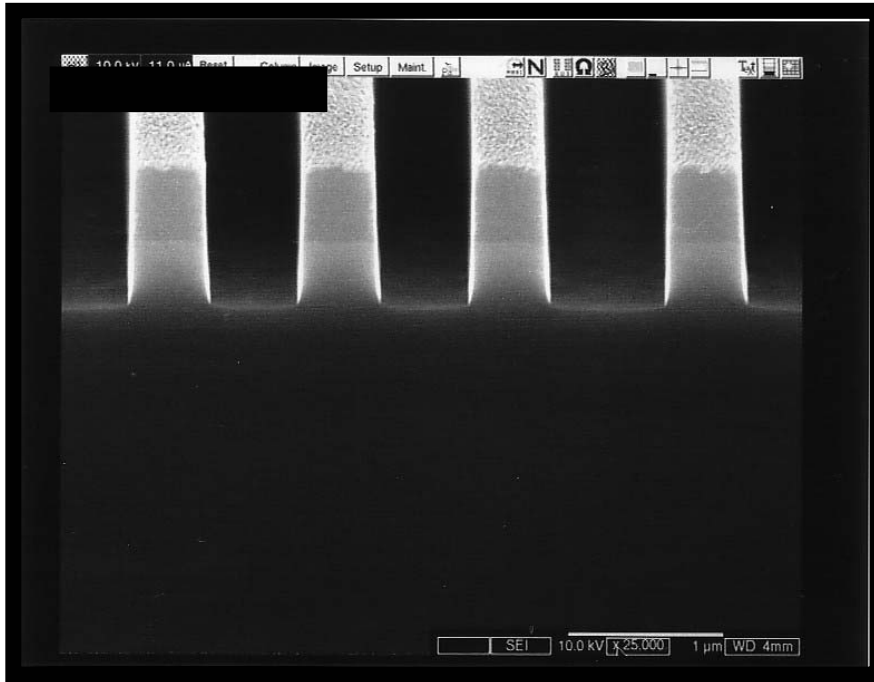
POST



Cleaning of Low k Wafers

(Whole 300 mm Wafer)

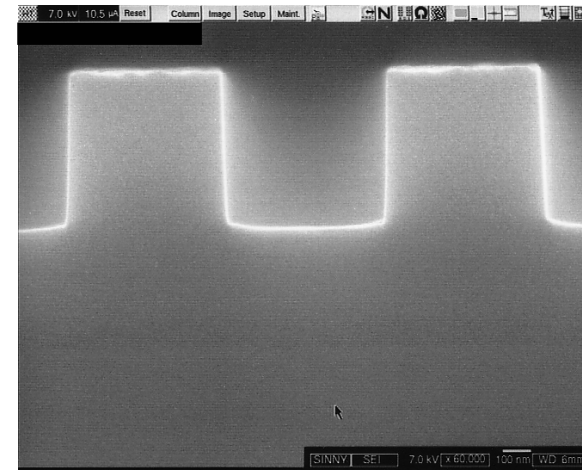
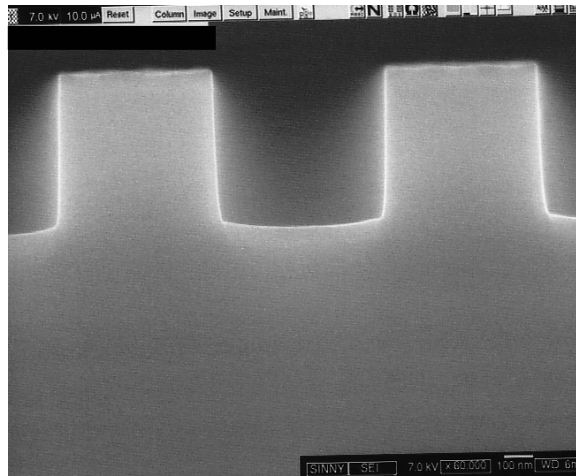
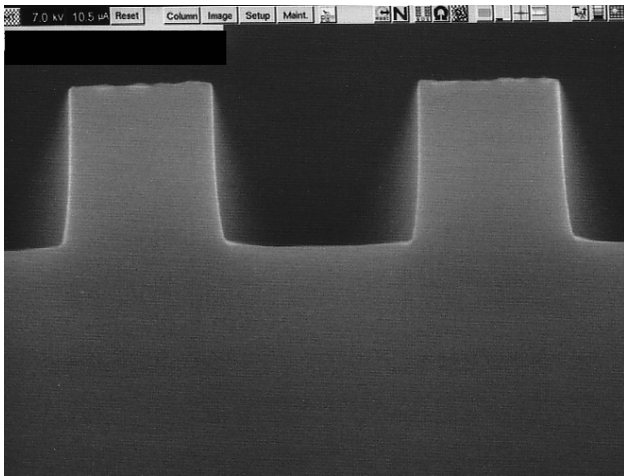
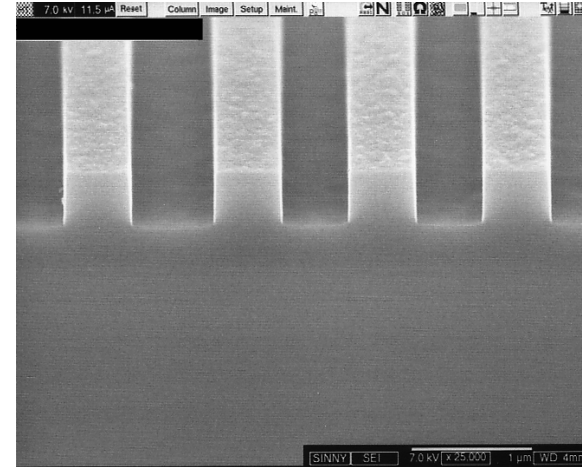
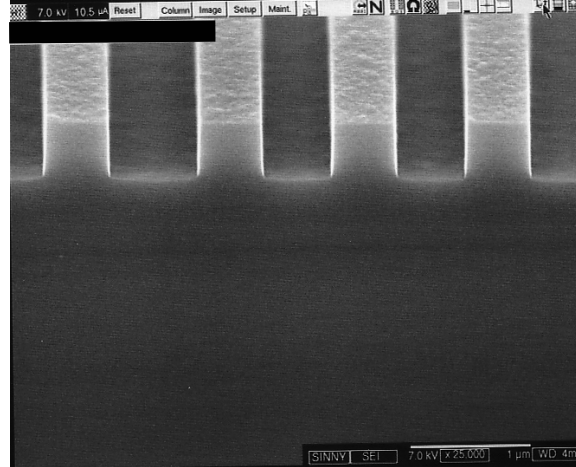
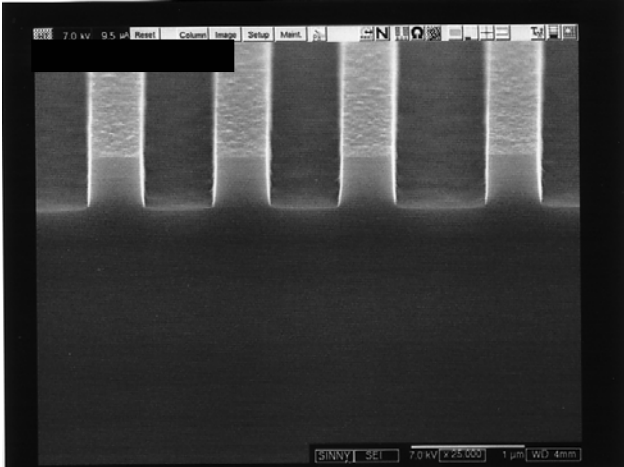
Before SCCO₂ Cleaning



Cleaning of Low k Wafers

(Whole 300 mm Wafer)

After SCCO₂ & Co-Solvent clean



Center

Mid-Radius

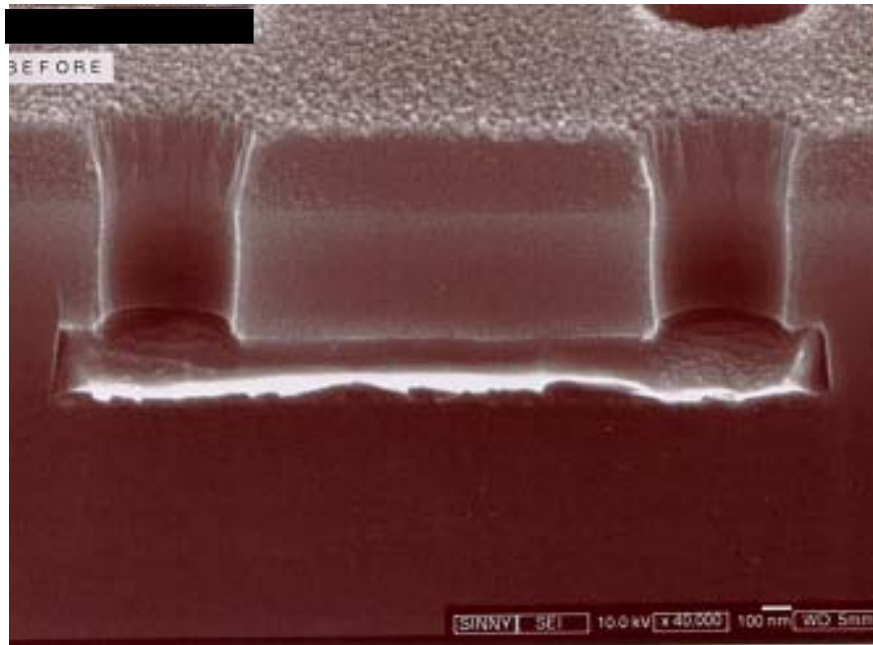
Edge

Results

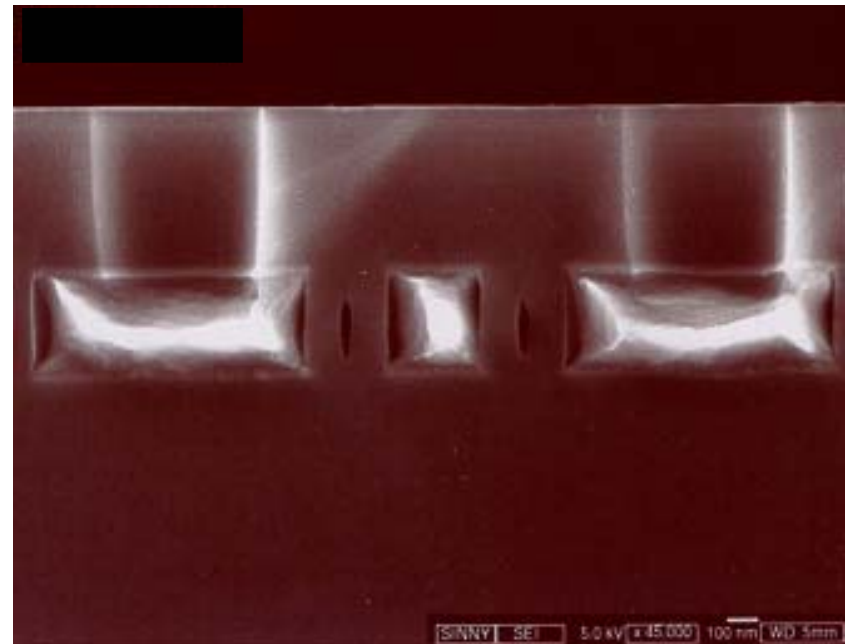
(Post metal etch clean)

Post metal etch (On Chips)

Pre



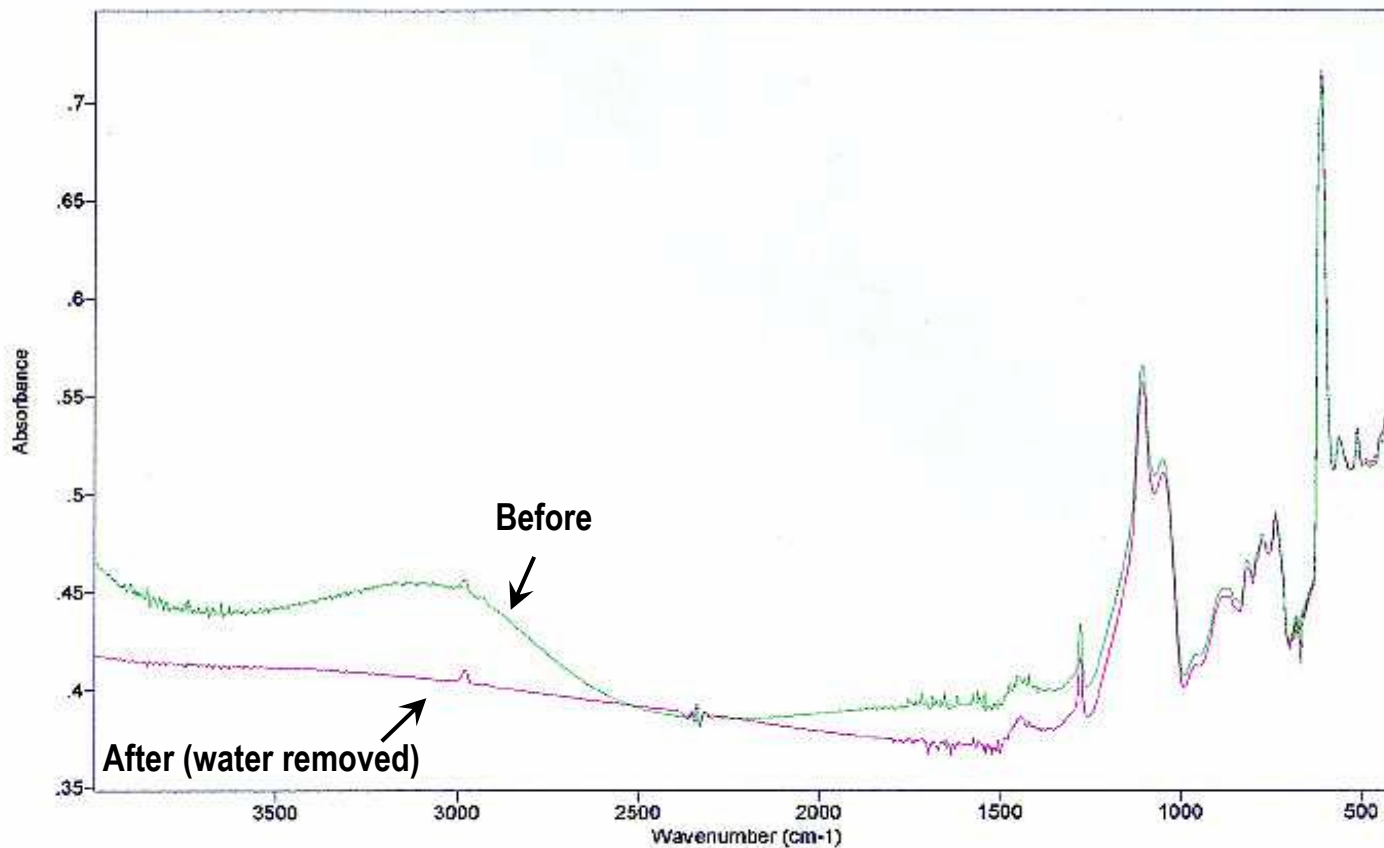
Post



Results

(k - Value Restoration)

Moisture Removal



File # 2 = SSI_MSQ1

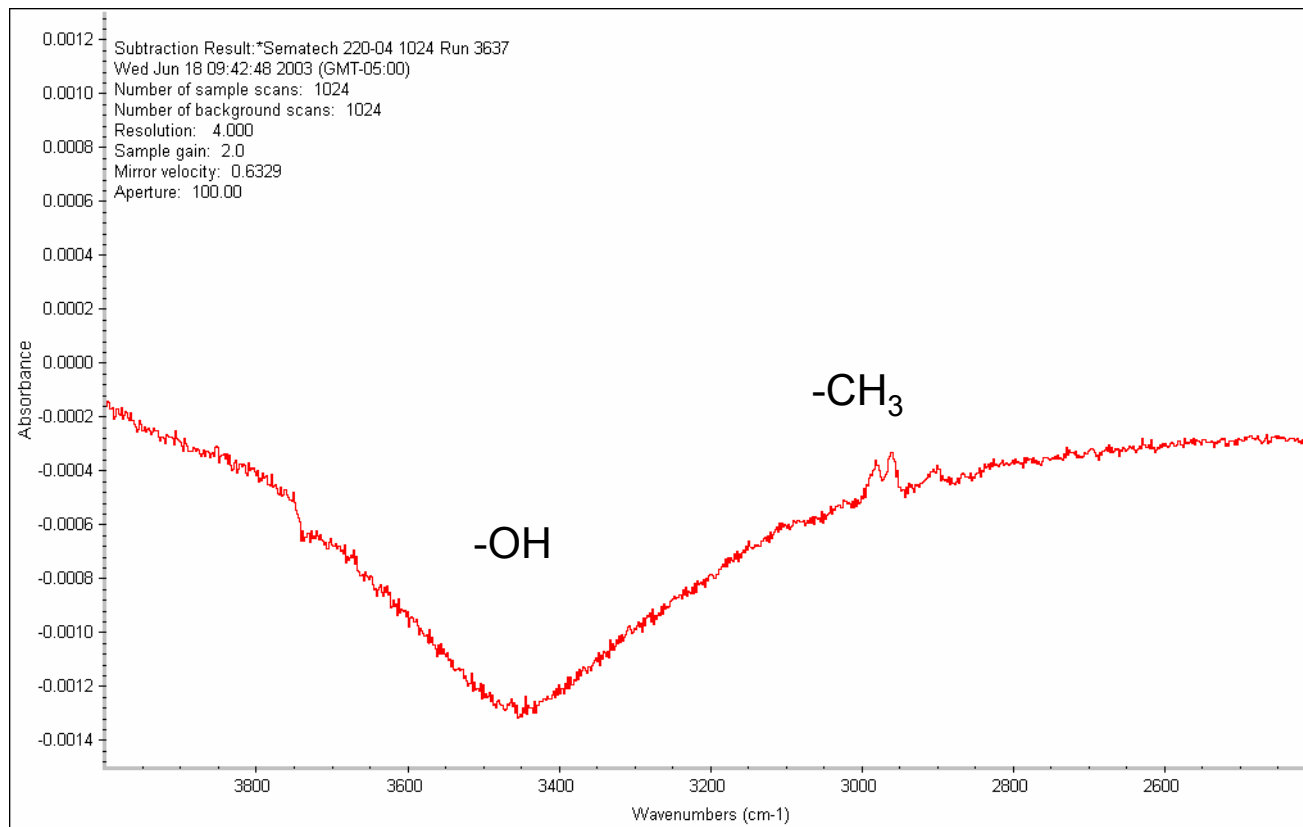
Number of Scans: 16

View Mode: Overlay

2/15/01 3:34 PM Res=4cm-1

Blanket JSR Post He/O₂ Ash

FTIR subtraction of Pre and Post SCCO₂ HMDS

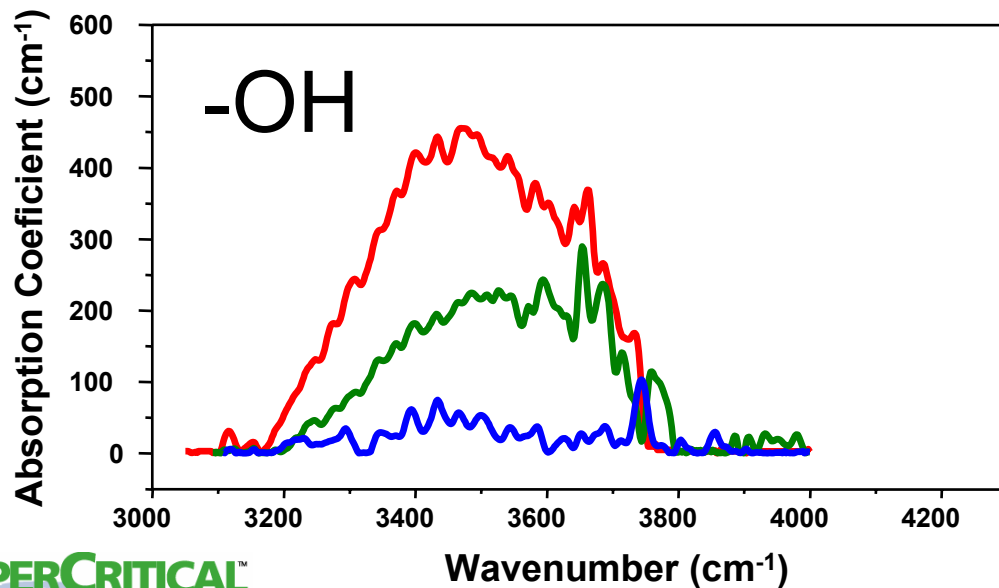
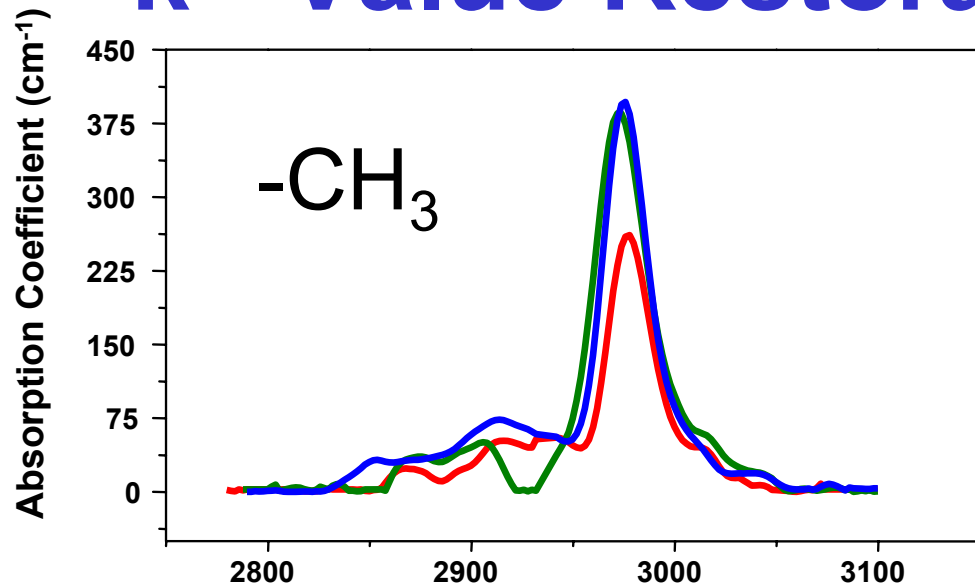


k-Value Restoration

- LKD films: MSQ1 (etched+N₂/H₂ plasma ashed)
MSQ3: Untreated (4000 A)
- Static SCCO₂ (3000psi for 30mins) + HMDS (2%)
- C-V (k): MIS, Ti metal gate, 10 kHz
- FTIR (-CH₃ and -OH concentrations)

Data collected by US BEOL Process Technology Group

k - Value Restoration (FTIR Results)



SCCO₂+HMDS →

- increase in -CH₃
- decrease in -OH

k - Value Restoration (k - Value Measurements)

Sample	K
MSQ3 (as received)	2.33
MSQ1 (ashed)	3.52
MSQ1: HMDS/SCCO ₂	2.43

Data collected by US BEOL Process Technology Group

Results

(Electrical Results)

ULK post ash: E-test

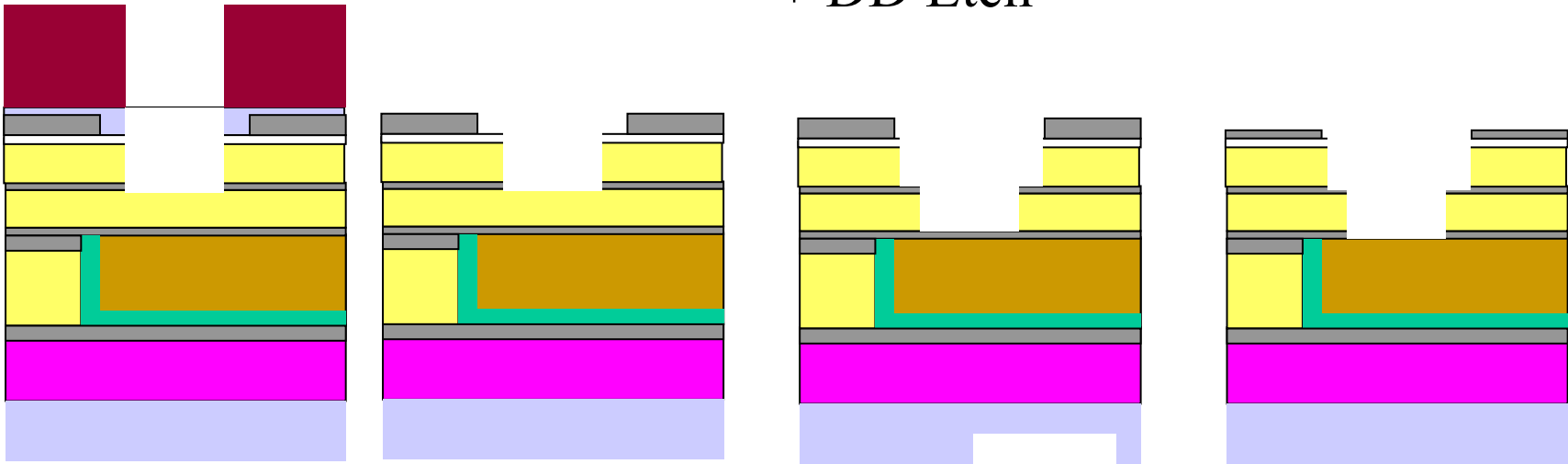
Sematech Trench First DD Flow

Etch Stop
Layer Etch

O₂ Ash

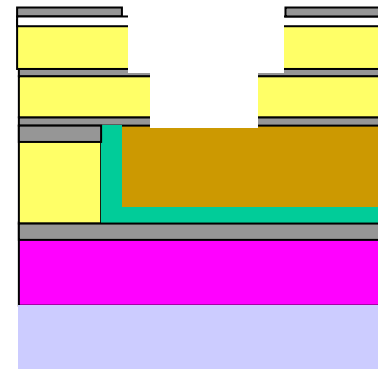
Ox HM Etch
+ DD Etch

Cu Cap Etch



A) PR200Z: DIW clean

B) SSI Alpha-1: MeOH/HMDS



E-test

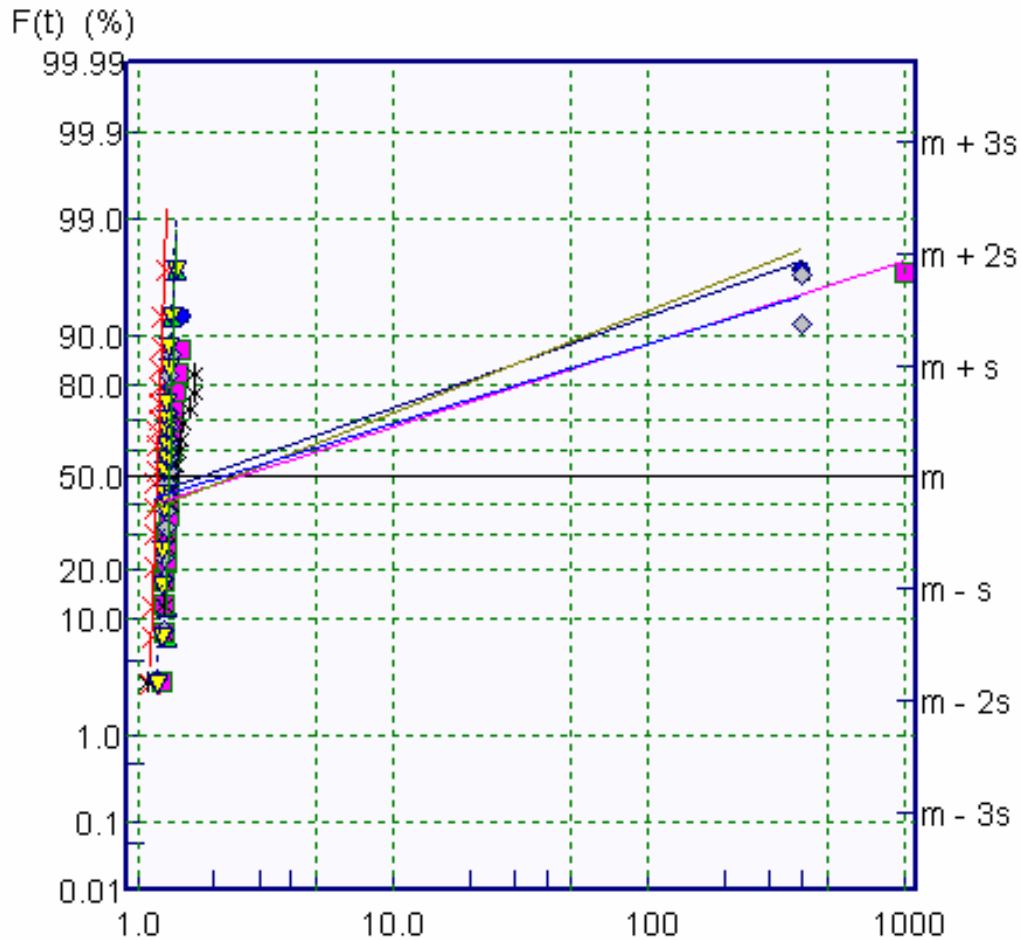
ULK post ash: E-test

Sematech JSR-DD Process Split

Lot No.	Wf.No.	Cleaning Tool	Cleaning Process
1092801B	21	SSI Alpha	CO ₂ Only
1092801B	22	SSI Alpha	CO ₂ + EtOH
1092801B	23	SSI Alpha	CO ₂ + MeOH
1092801B	24	SSI Alpha	CO ₂ + MeOH + HMDS
2091712	13	PR200Z	DIW
2091712	14	PR200Z	DIW
2091712	15	PR200Z	DIW

M2 Resistance

0.25um 64.8cm Long Serpentine



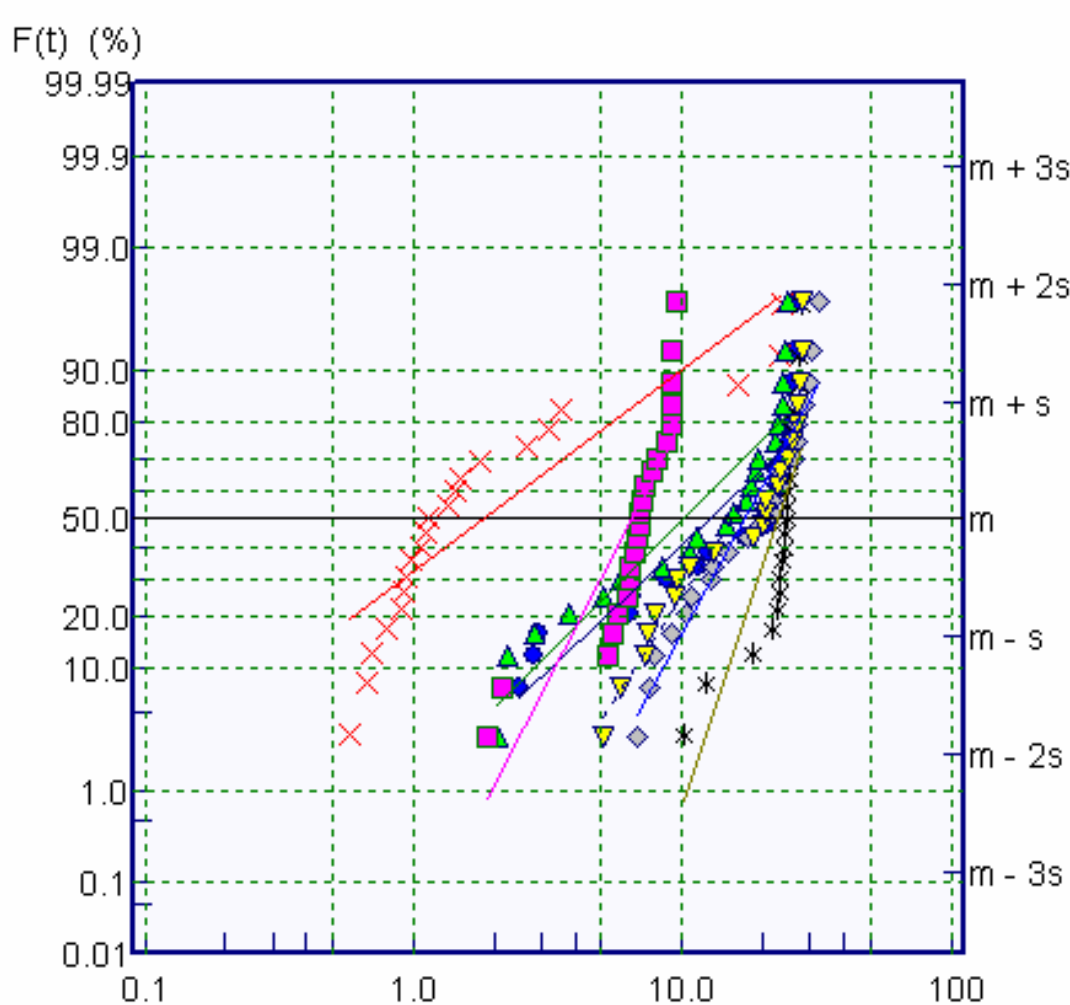
Median rank method

No.	Mark	Object name
1	●	CO2
2	×	CO2+EtOH
3	▲	CO2+MeOH
4	■	CO2+MeOH+HMDS
5	*	DMV-2091712-13
6	◇	DMV-2091712-14
7	▼	DMV-2091712-15

No difference in Resistance between the two lots. This means Trench size of the two lots are the same.

M2-M2 Leakage

(0.25/0.3um, 64.8cm Long Serpentine)



Median rank method

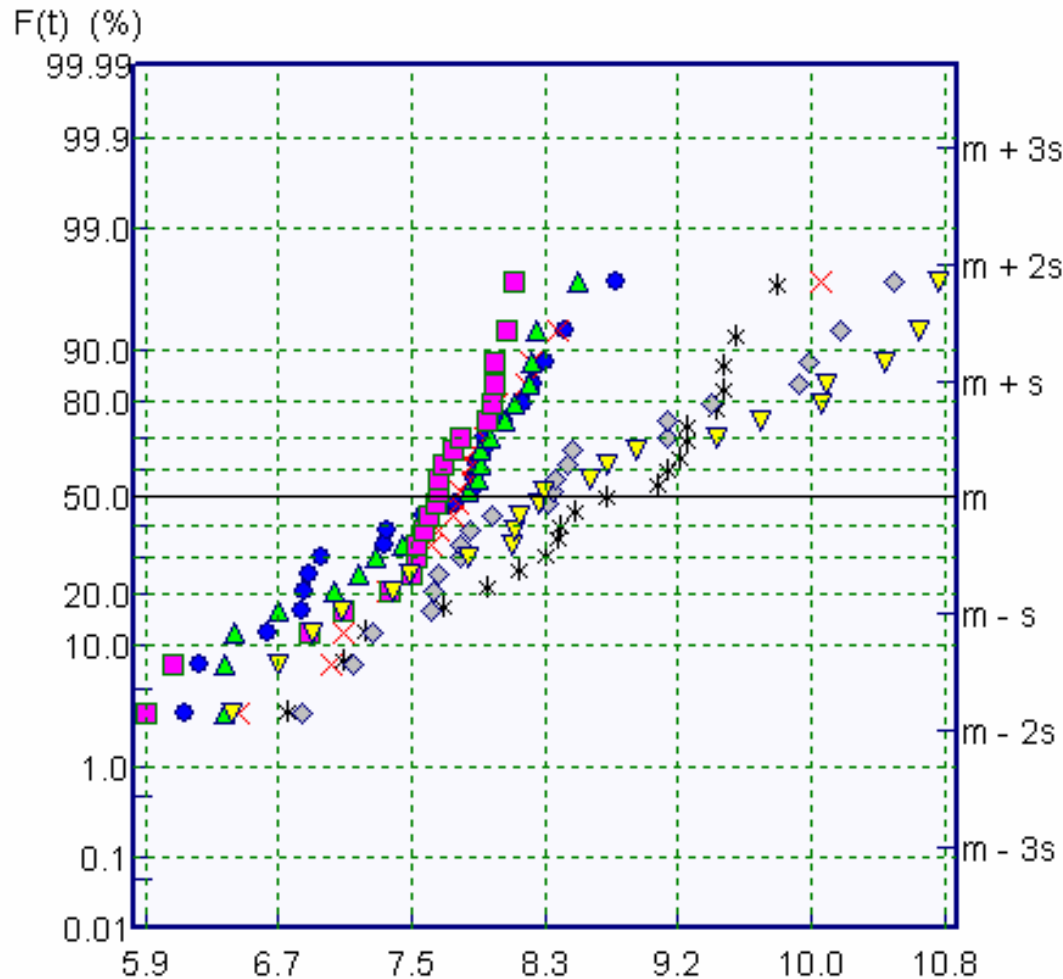
No.	Mark	Object name
1	●	CO2
2	×	CO2+EtOH
3	▲	CO2+MeOH
4	■	CO2+MeOH+HMDS
5	*	DMV-2091712-13
6	◆	DMV-2091712-14
7	▼	DMV-2091712-15

CO₂ splits show lower leakage current.

HMDS split has tighter Distribution than others.

M2 Capacitance

(0.25/0.3um, 114 Fingers, 9.12cm Perimeter)



About 10% lower capacitance in CO₂ splits.

JSR Post ash E-test data

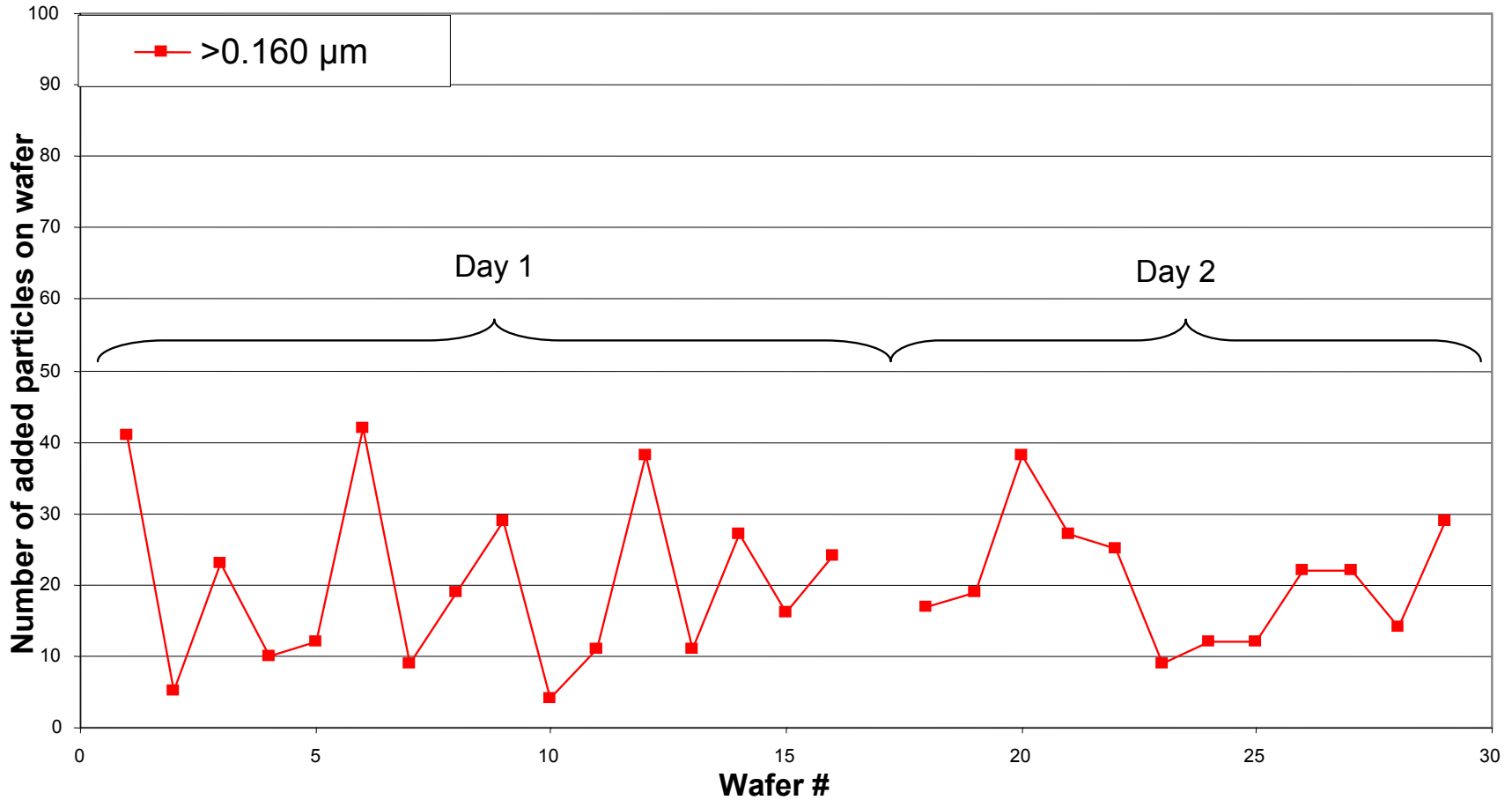
- SCCO₂ treatment
 - EtOH used in SCCO₂ treatment was not semiconductor grade, i.e. this data not reliable.
- Despite no clean before SCCO₂, improved E-test data was obtained

Results

(Defects)

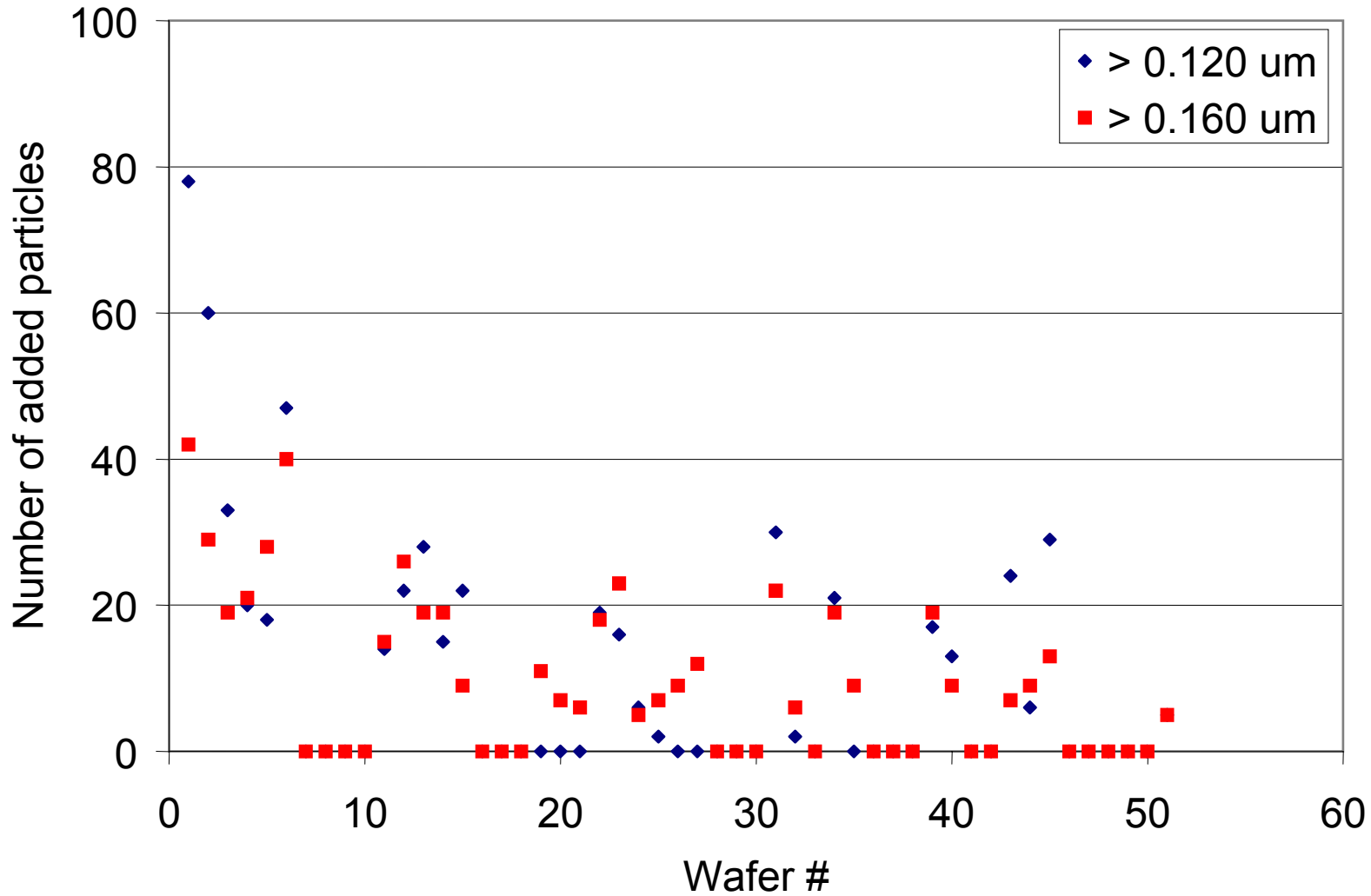
Particle Data from α - Tool

(CO₂ & Process Chemistry)

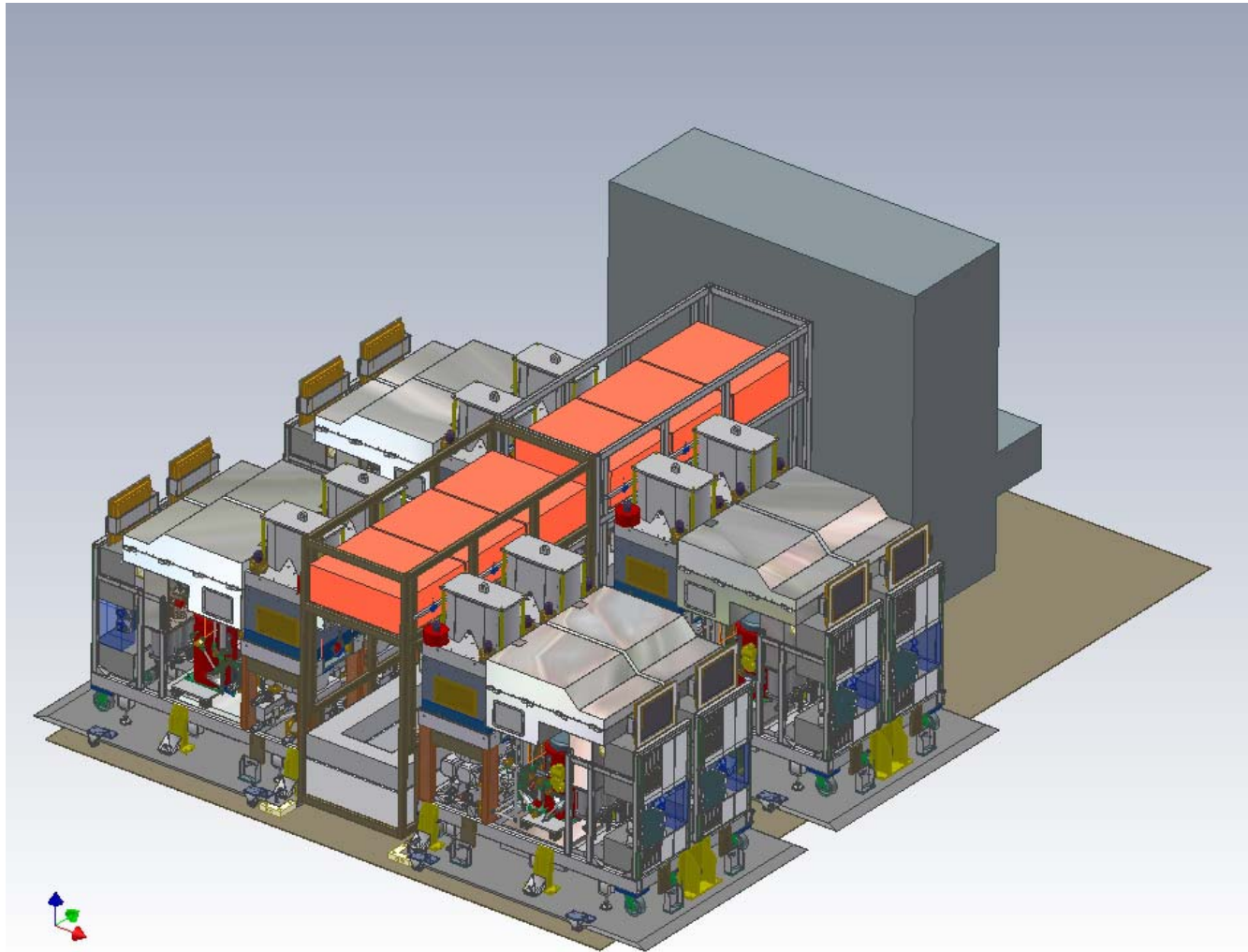


Particle Data from MCM 300

(CO₂ only)



β Tool MCM300



β Tool



1300 lb/hr High Pressure Skid



Recycle Skid



- CO₂ Purification and Delivery System
- Recycles and treats spent CO₂ exhaust
- Recovers CO₂ for reuse
- Separates and removes heavy organic compounds
- Delivers CO₂ at 1000 psig
- 100 lb/hr capacity
- CO₂ supplied from dewar at 300-400 psig
- Purification Process
 - Expansion
 - Distillation
 - Compression
 - Liquefaction

Summary

- Supercritical CO_2 based cleaning is effective for removing photoresist and etch/ash residue
- No surface tension allows for cleaning $<0.10 \mu\text{m CD}$
- k-value restoration by repairing CDO and drying
- Process is compatible with porous Dielectrics
 - No Damage
 - Moisture Removal
 - Enhanced electrical properties