Low Concentration Fluoride Chemistries For Cleaning Sub-0.25 Micron IC Devices

Semi-Aqueous Chemistry (SAC™)

US Patent 6,235,693; 6,248,704

R. Small, Ph.D., Mel Carter, Ph. D., J. Cheng, Ph.D.
B. Patel, M. Cernat, B. Hanson

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Updated: 5/25/01

EKC Technology

- A Specialty Chemical Manufacturer
- Develops Efficient CMP and Cleaning Processes
- Manufacturers Novel CMP Products
  - Tungsten CMP Slurries
  - Copper, Oxide and Other Slurries
- Manufacturers Several Families of Removers
  - Aqueous HDA Chemistries
  - Water Rinsed SAC Chemistries

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SAC™ Design Criteria

- Remove post etch residues @ 20°C to 30°C.
- Buffered chemistries with stable pH
- Low fluoride concentrations (<1 %)
- Designed for all types of cleaning equipment.
  - Spray tools: SEZ, FSI and SemiTool
  - Wet benches: Akrion and others
- Low viscosity for equipment and filter capability.
- Ability to remove post etch residues without attacking the silicon dioxide.

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“Green Chemistries”

- Principles
  - Look at potential hazards instead of exposure
  - Economically driven not resource draining
  - Minimum regulated content
  - Use Problem Avoidance approach
  - Life time impact considered at design stage

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Green Chemistry Criteria

- Additional Criteria for material selection
  - Raw material should be environmentally friendly
  - Materials should be of reduced toxicity
  - Starting materials should be renewable
  - Starting material might be ‘waste’ from another process.

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SAC™ Product Goals

- Compatible with most low-k dielectric materials
- Minimum W-Plug corrosion
- Ability to remove surface mobile ions
- Non-hydroscopic formula
- Room temperature operation
- Water rinseable (no intermediate rinse required)
- Environmentally friendly products

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SAC^{TM} Physical Properties

- pH: ~9
- Refractive Index: 1.41
- Viscosity: 1-2 cp
- Density: ~1
- Solubility in water: complete
- Physical state: liquid
- Appearance: clear
- Flash point: >110°C

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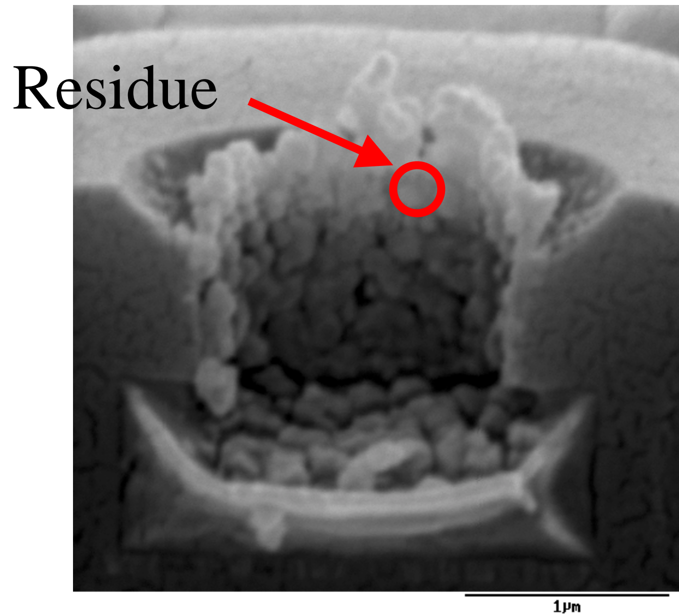
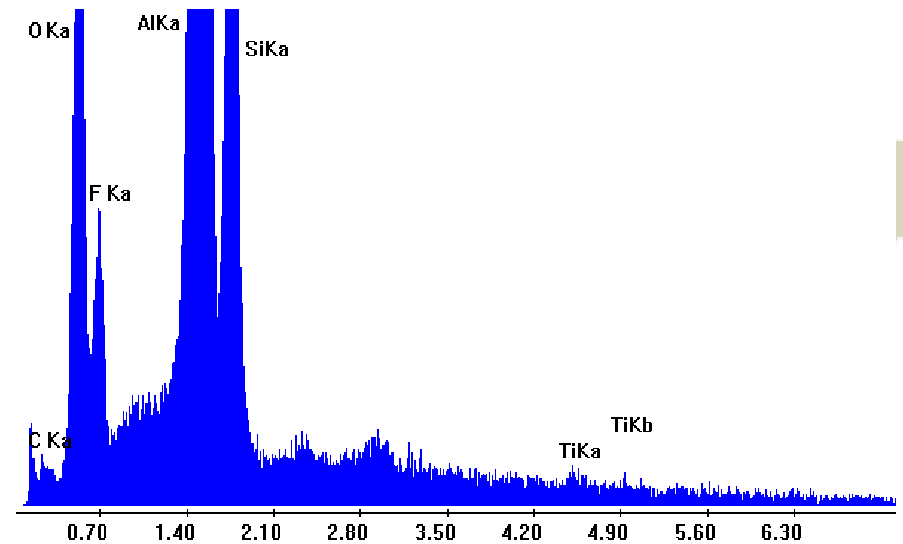
Via Residue Samples*





Oxide-SOG-TEOS via (Ø1.3 - 1.7µm) etched with Ar / CHF_3 / CF_4 chemistry stopping on AlSiCu

EDX spectrum of post-via-etch residue ("polymer veil")

* S. Lutter, Ph. D. Dissertation, Fachhochschule Regensburg, GR

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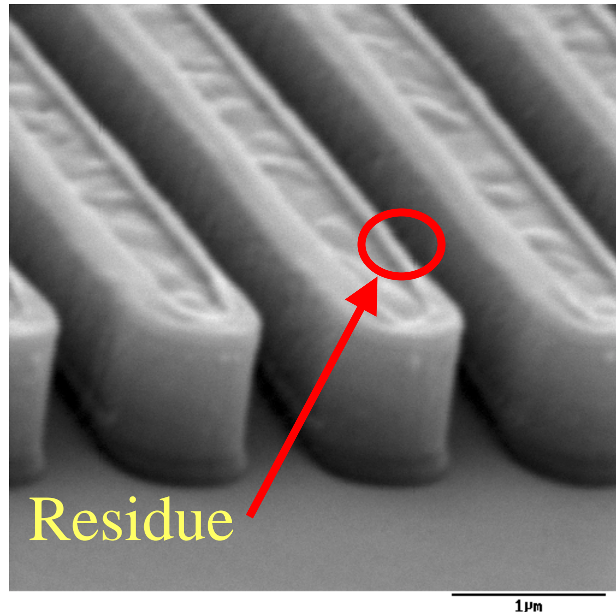
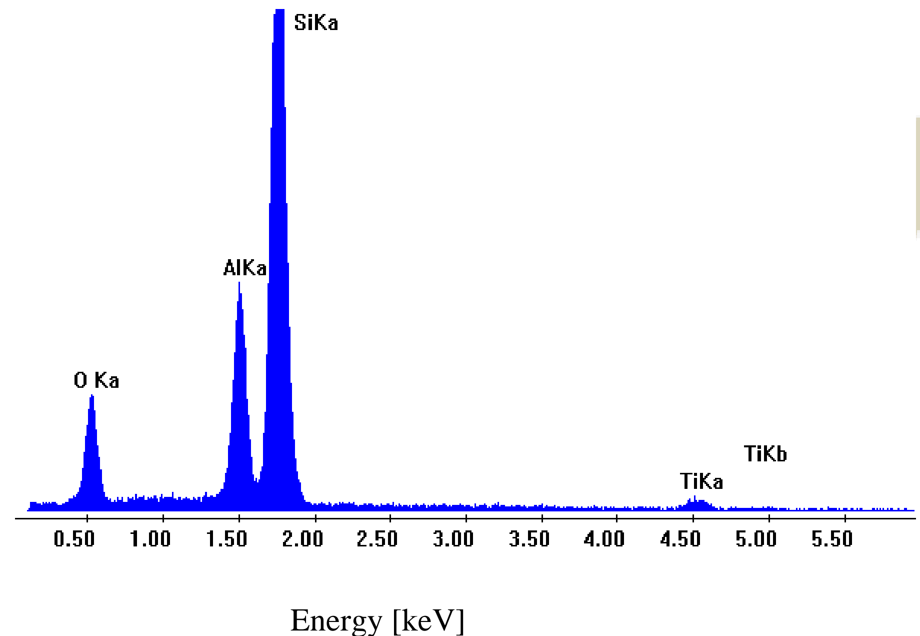
Metal Residue Samples





0.8µm Ti/TiN-AlSiCu-TiN lines (0.4µm spacing) etched with Cl_2 / BCl_3 chemistry

Energy [keV]

EDX spectrum of post-metal-etch residue

* S. Lutter, Ph. D. Dissertation, Fachhochschule Regensburg, GR

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SAC™ Chemistries

- SAC™ chemistries use different principles for removing PER (post etch residue)
- The PER are not actively "etched" during the cleaning process as with HDA™ chemistries.
- The SAC™ chemistries are designed to use low concentrations of active fluoride species.
- The PER's are converted to new reactive species with the SAC™ chemistries.

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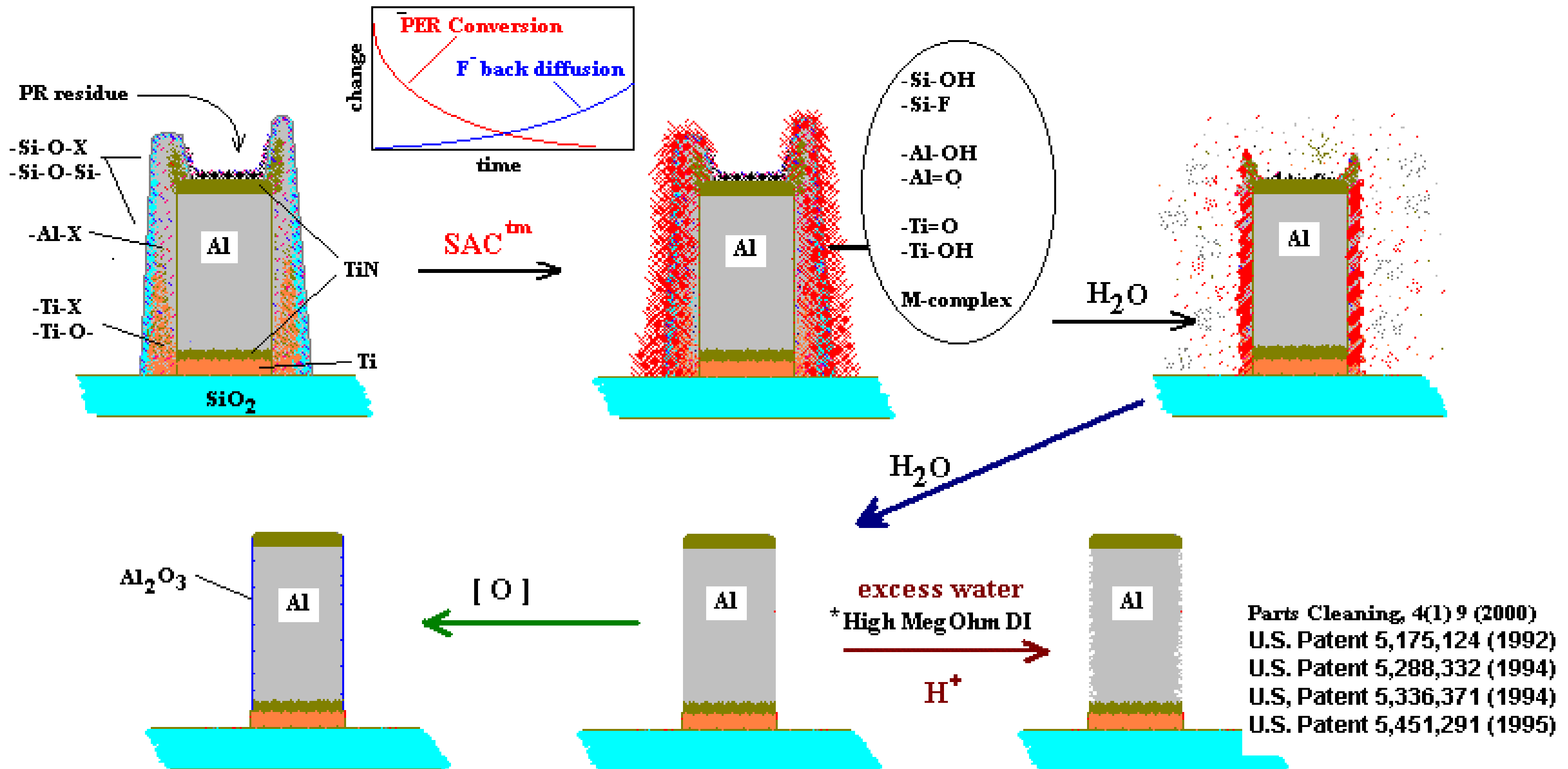
Proposed SAC™ Mechanism



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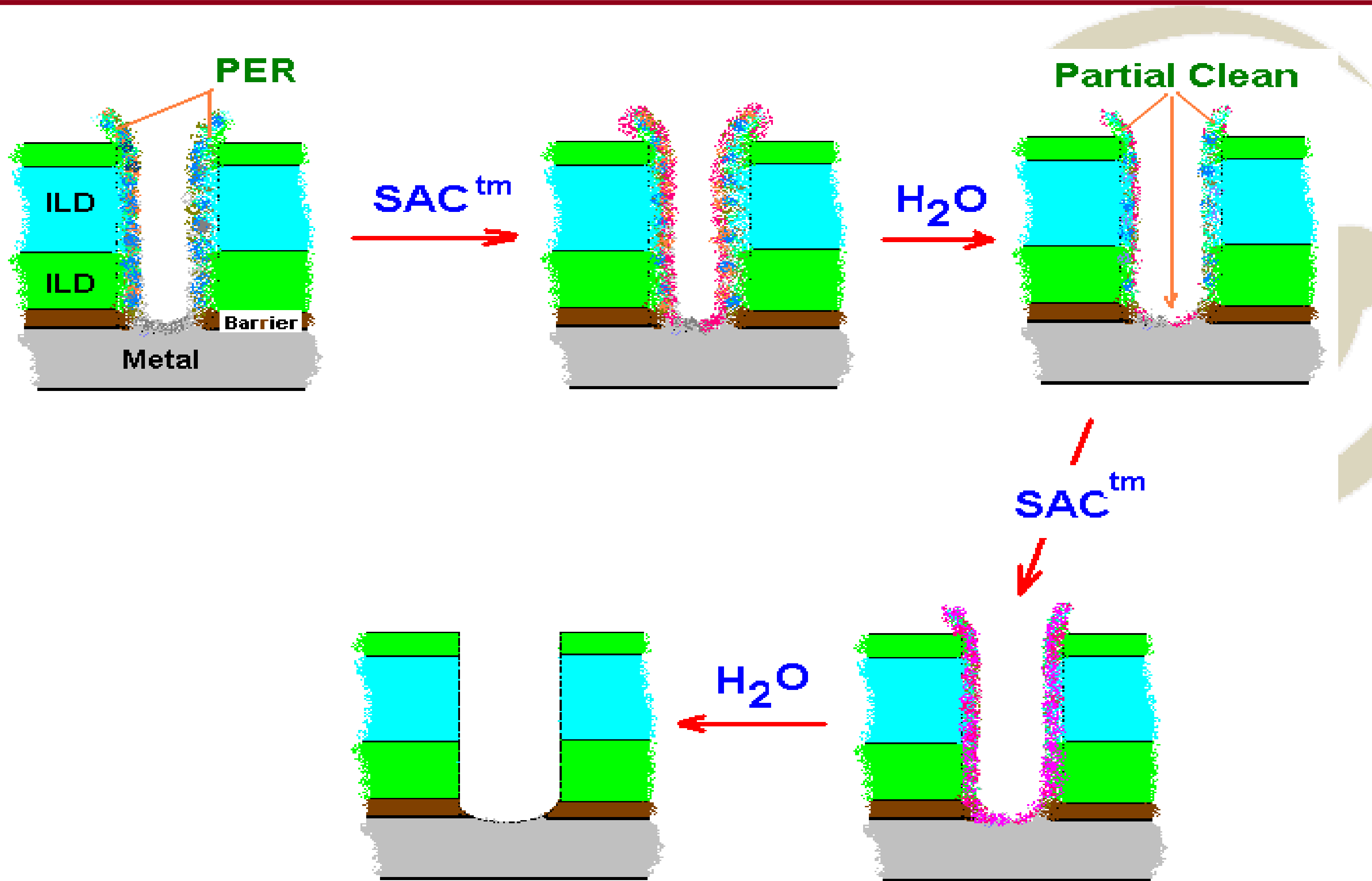
Via Cleaning Method for Single/Spray Tools



Tested with SEZ, FSI and SemiTool

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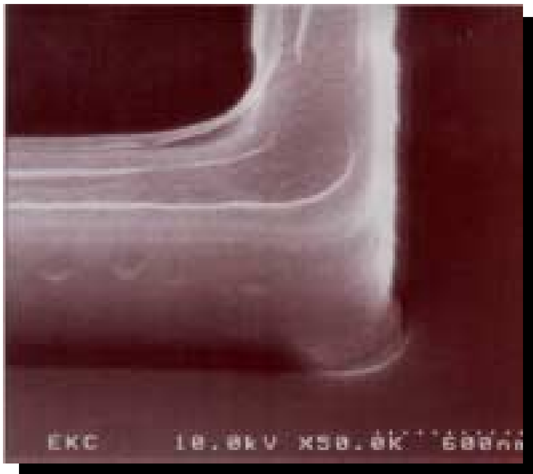
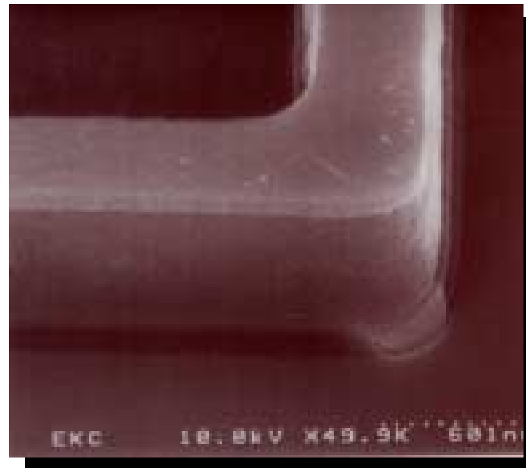
W Plug Compatibility in Unlanded Applications

After Etch

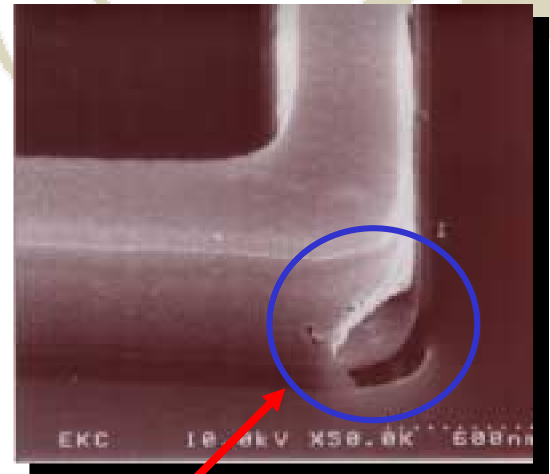


After EKC640™
Temp.: Ambient
Time: 20 min.



Outstanding Clean Result

Failure Mode
Conventional Remover
Temp.: 70°Time: 20 min.



W Plug eroded

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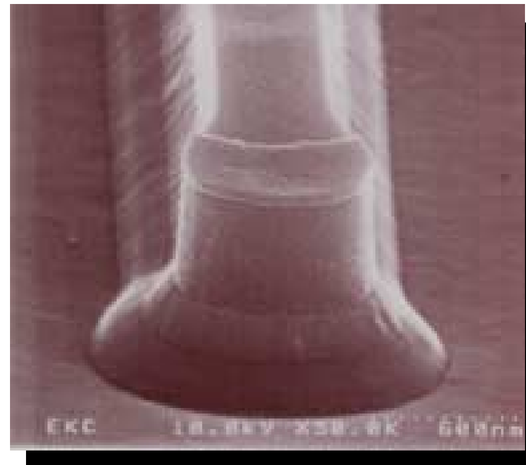
SAC™ EKC640™ Metal Cleaning Results

After Etch

After EKC640™
Temp.: Ambient
Time: 30 sec.



After EKC640™
Temp.: Ambient
Time: 5 min.

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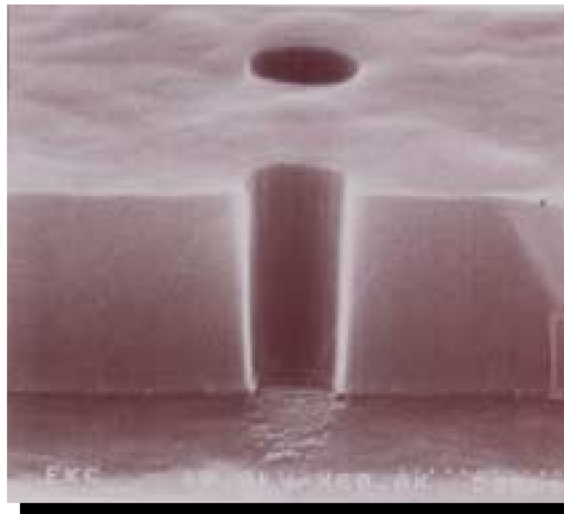
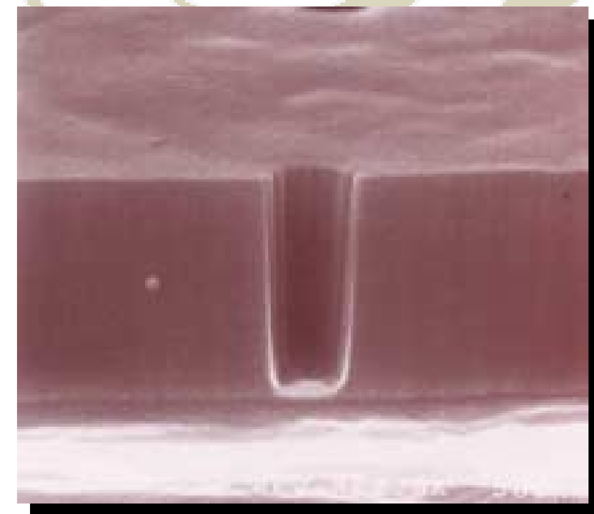
EKC640™ Via Cleaning Results

After Etch

After EKC640™
Temp.: Ambient
Time: 30 sec.



After EKC640™
Temp.: Ambient
Time: 5 min.



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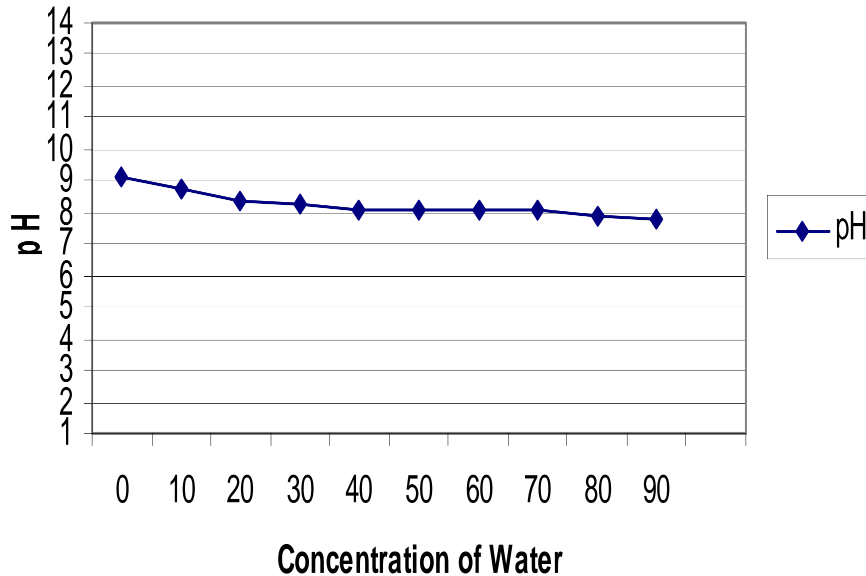
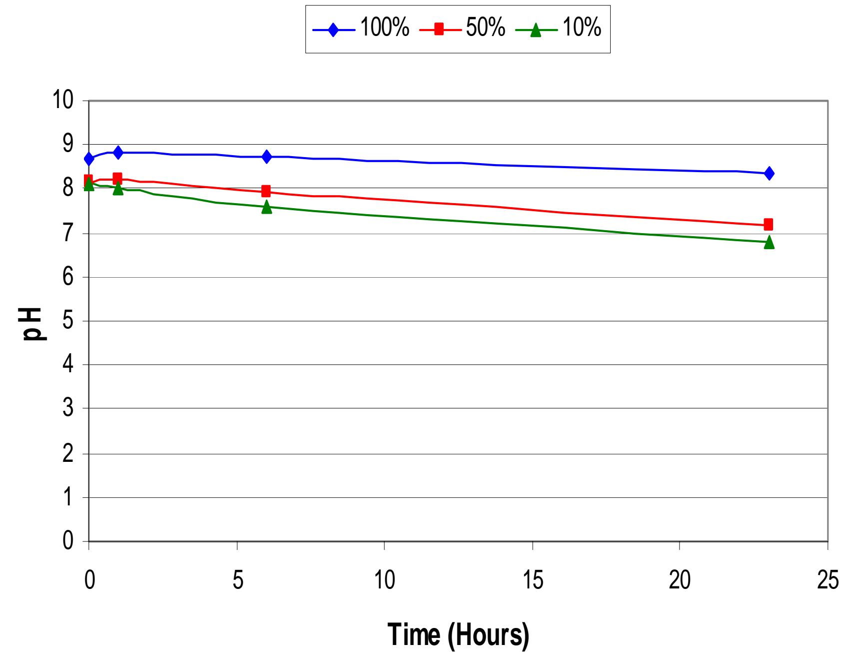
EKC640™ pH STUDY





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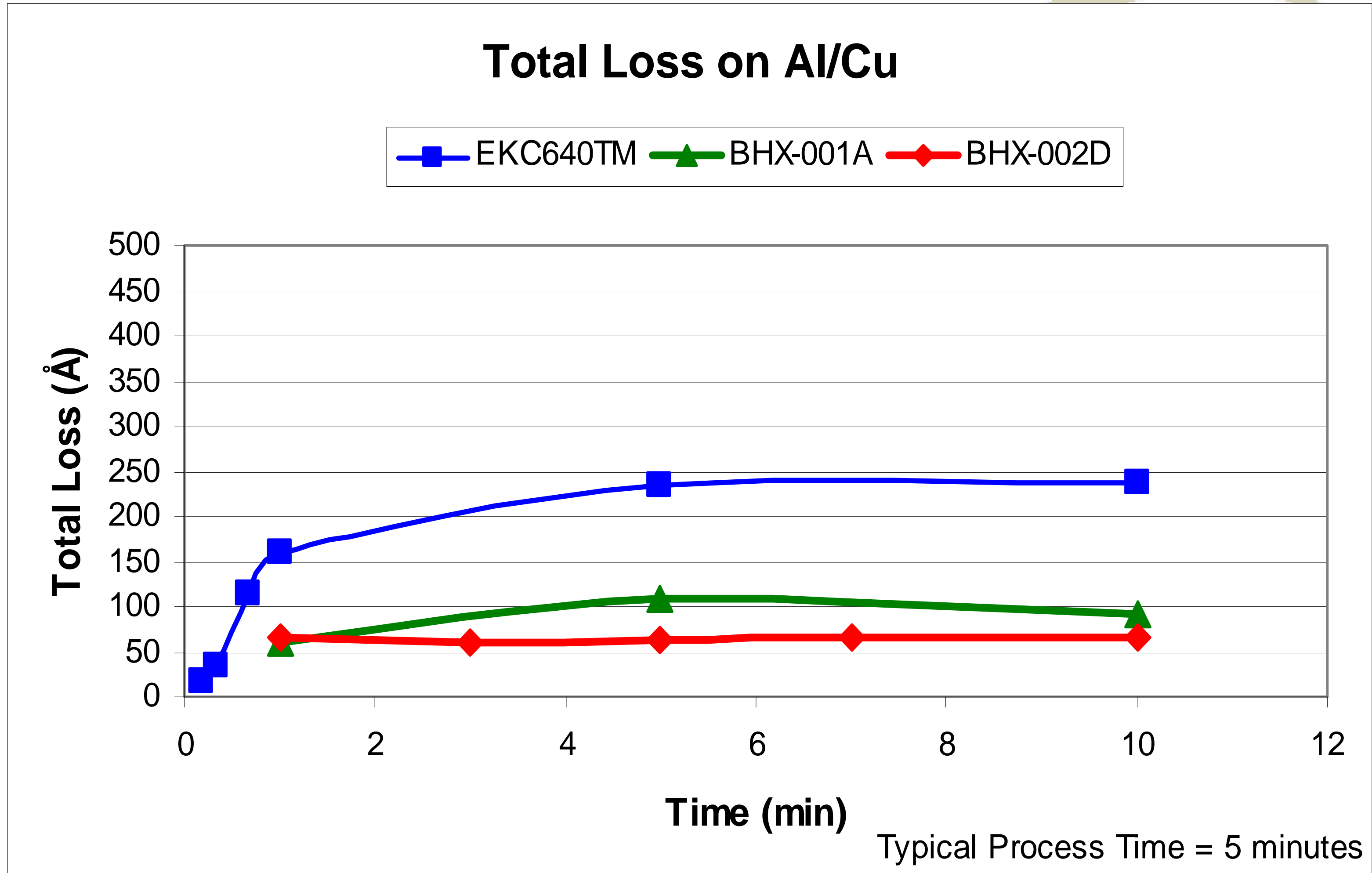
Al/Cu Etch Rates: SAC™ Chemistries



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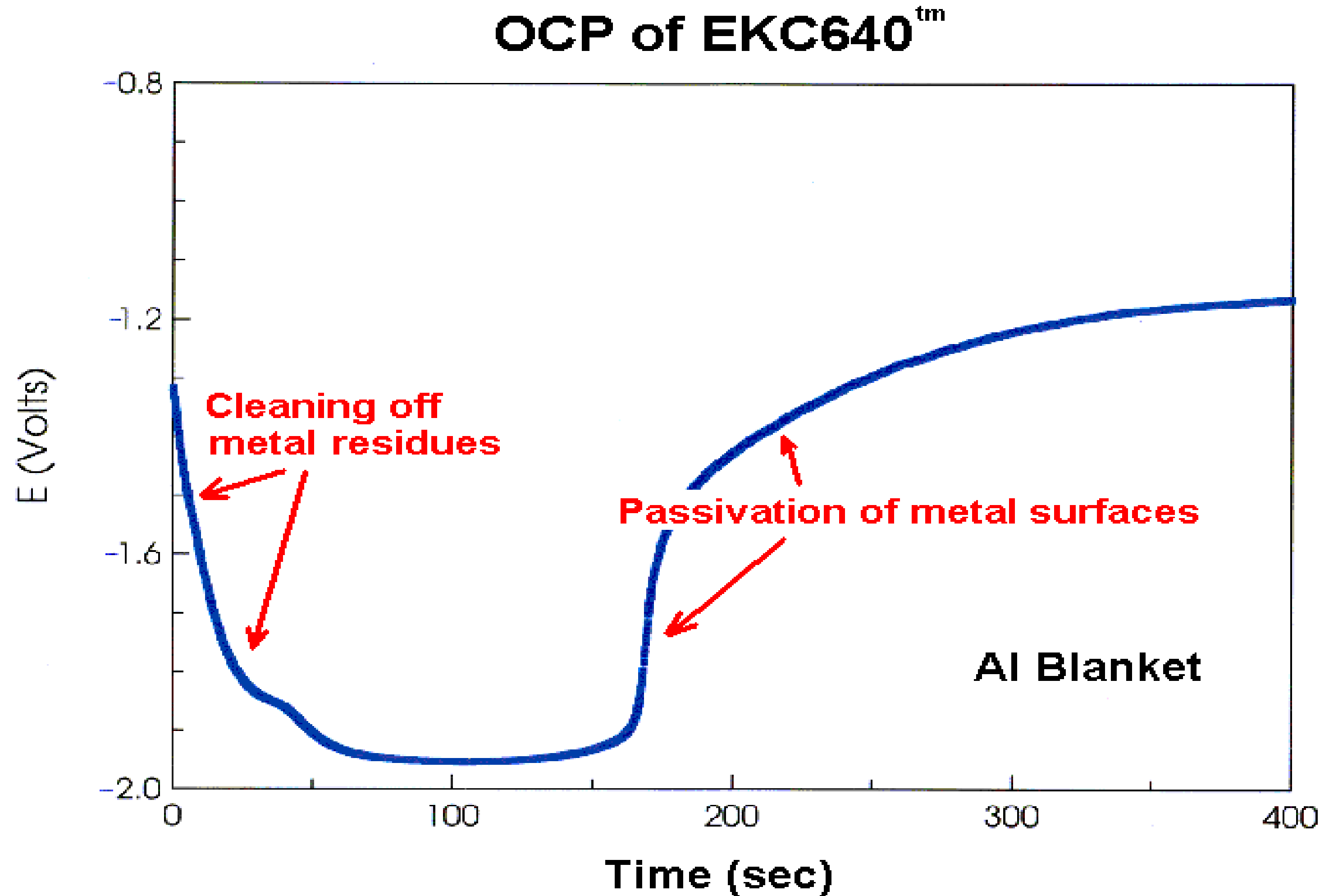
OCP of EKC640™



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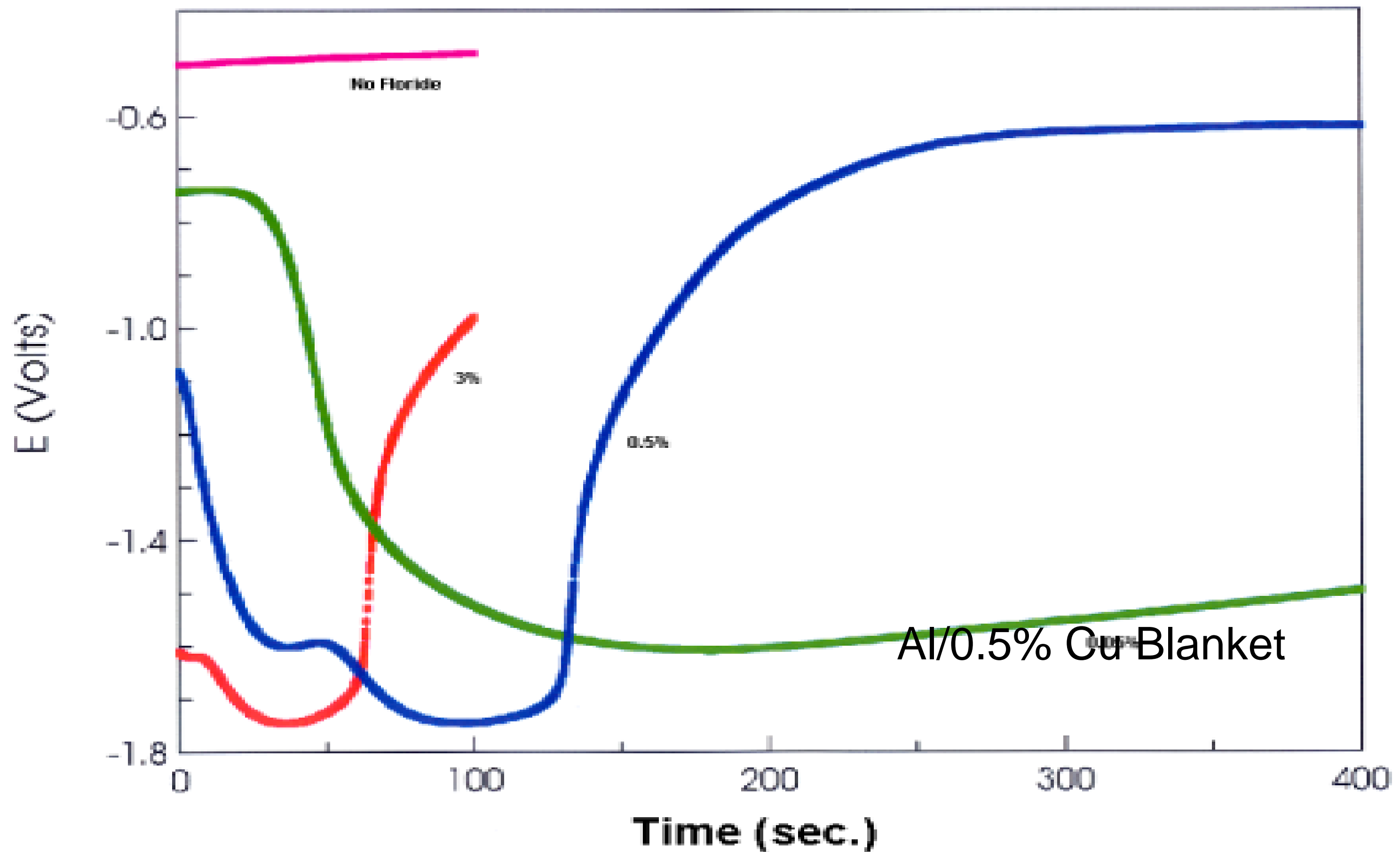
OCP vs Fluoride Concentration



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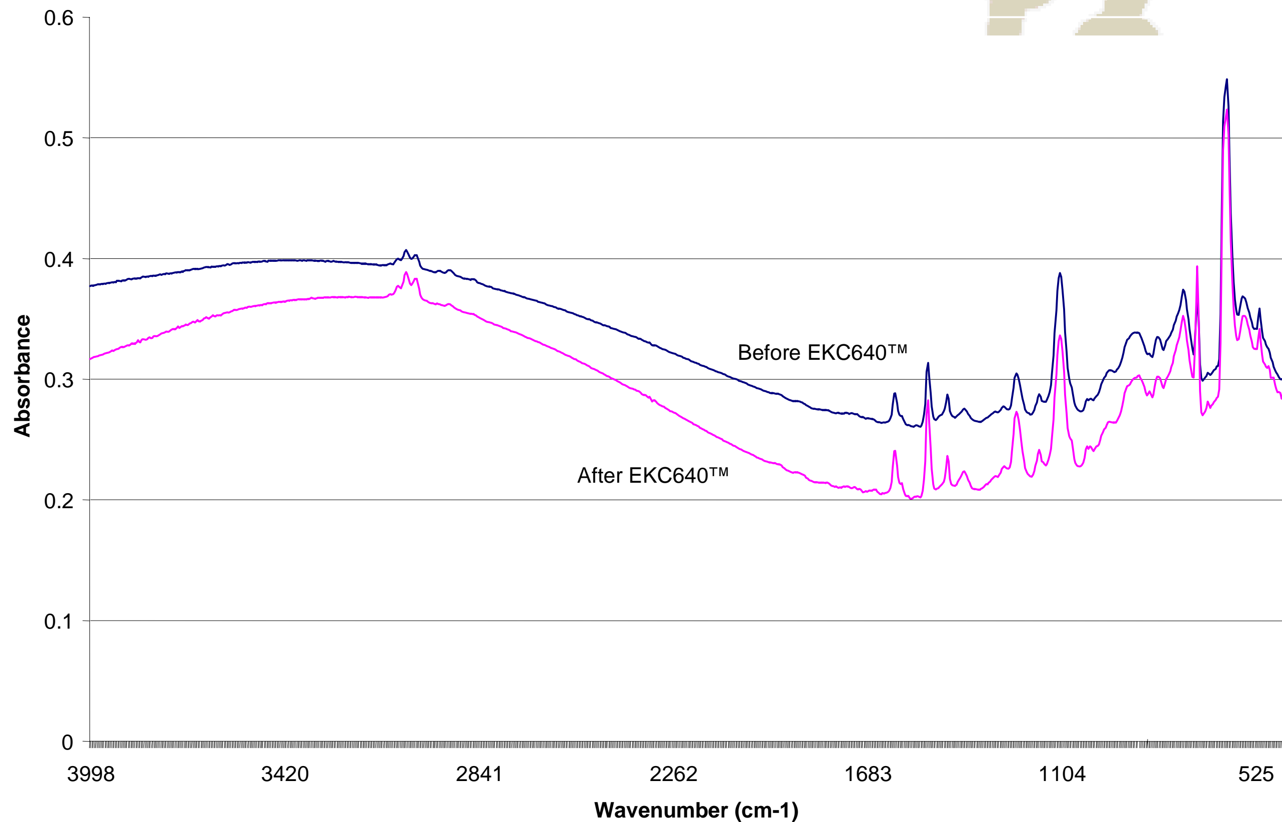
Compatibility with Low-k Dielectrics

FT-IR Analysis of SiLK 450 Before and After Processing in EKC640™ for 5 Minutes at 23°C



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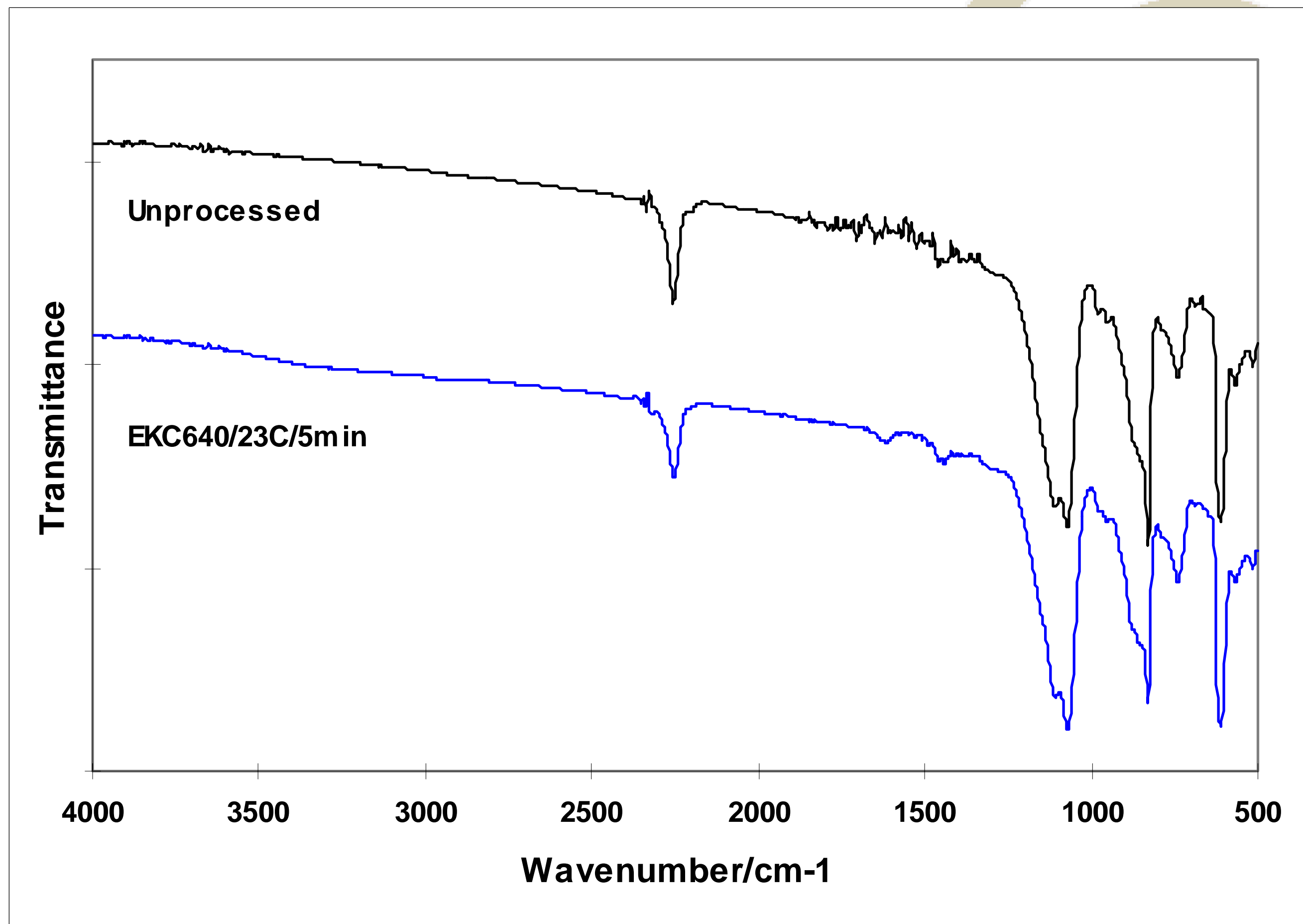
EKC640™ Compatibility with FOx®



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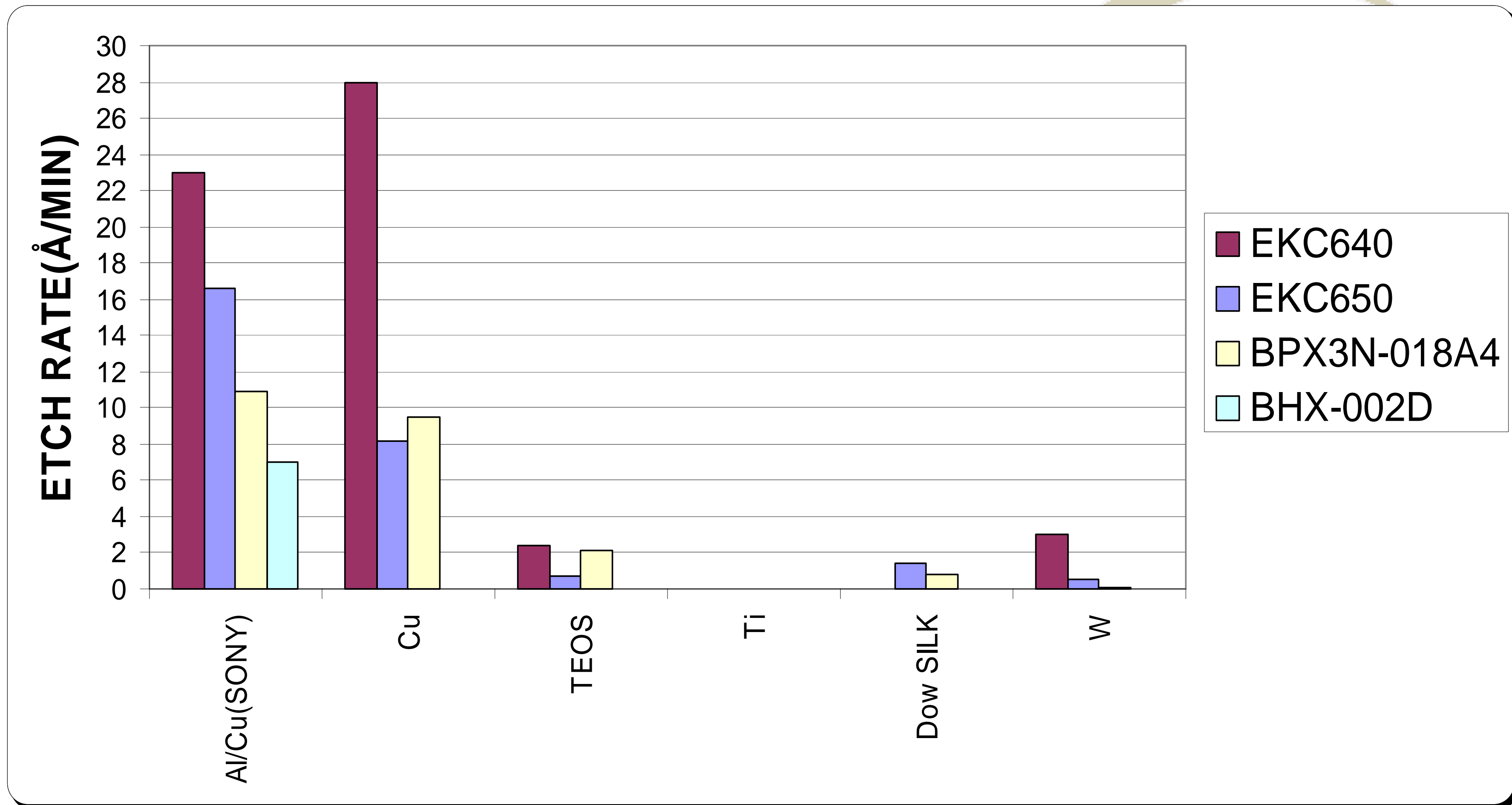
Etch Rate Data (SAC™ Chemistries)



Dynamic stirring at 25C

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Blanket Wafer Etch Rates in Fluoride Chemistries

Film Type	EKC640™ [1] (Å/min)	BHX-002D [2] (Å/min)
AlCu	8	3
Ti	< 0.1	< 0.1
W	< 0.1	< 0.1
Cu	0.1 - 6	0.1 - 3
TEOS	4	2 - 5
BPSG	2 - 4	2 - 5

(1) Testing was performed using a static bath.

(2) Testing was performed using a dynamic bath.

Operating conditions for tests conducted at ambient temperature for 30 minutes.

Note: Values may change with different substrates and process conditions. This information is intended as a relative guide only.

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Blanket Wafer Etch Rates in Fluoride Chemistries

Film Type	EKC640™ [1] (Å/min)	BHX-002D [2] (Å/min)
Silk	~ 0	~ 0
Flare	~ 0	~ 0
MSQ	+ 10	3 - 5
BCB	~ 0	T.B.D.
SPEEDFILM	5 - 7	N.D.
LPSZ - R	7	N.D.
HOSP	10	T.B.D.
Flare 2	0.4 - 2	T.B.D.
FOX	7-54	T.B.D.

[1] Testing was performed using a static bath.
[2] Testing was performed using a dynamic bath.

Operating conditions for tests conducted at ambient temperature for 30 minutes.

Note: Values may change with different substrates and process conditions. This information is intended as a relative guide only.

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SAC™ Material Compatibility

Temperature: Ambient Room Temperature | Exposure Time: 5 days

All of these materials passed

- Polypropylene
- PVDF
- PFA
- PVC
- Kalrez 1050LF; Kalrez 2037; Kalrez 4079; Kalrez 8201
- PEEK
- Chemrez 550
- SEP21 treated 316 SS
- Electropolished 316 SS

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SAC™ Design Criteria

- **Ability to remove post etch residues @ 20°C to 30°C** ✓
- **Process times: 1 to 25 minutes** ✓
- **Buffered semi-aqueous chemistries with stable pH** ✓
- **Designed for all types of cleaning equipment**
  - Spray tools: SEZ, FSI and SemiTool ✓
  - Wet benches: Akrion and others ✓
- **Low viscosity for equipment and filter capability** ✓
- **Ability to remove post etch residues without attacking the oxides** ✓
- **No W-Plug corrosion** ✓

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SAC™ Design Criteria cont.

- **Compatible with most low-k dielectric materials** ✓
- **Ability to remove surface mobile ions** ✓
- **Does not absorb moisture during usage** ✓
- **Room temperature operation** ✓
- **Water rinseable (no intermediate rinse required)** ✓
- **Environmental friendly** ✓
- **Excellent bath life and loading create low Cost of Ownership (CoO)** ✓

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General Conclusions

- **Cleaning effects depended on type and concentration of fluoride species and on the solvent system.**
  - Careful control of ionic activity can produce very specific cleaning chemistries (“silver bullets”).
  - Cleaning kinetics can be better matched to the equipment (wet benches, spray tools, single wafer tools).
  - Good performance on many structures with mild process conditions (Al/Cu, Ti, W, Cu).
  - Ability to remove surface mobile ions.
  - Low etch rates.
  - More options for rinsing (conserve DI water).

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