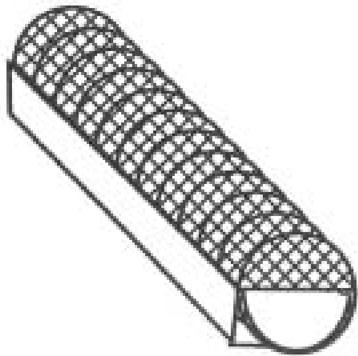
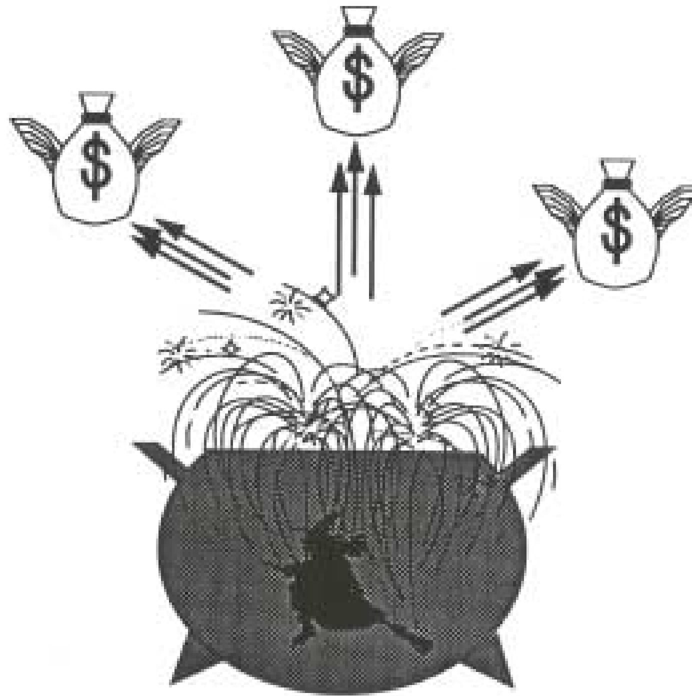
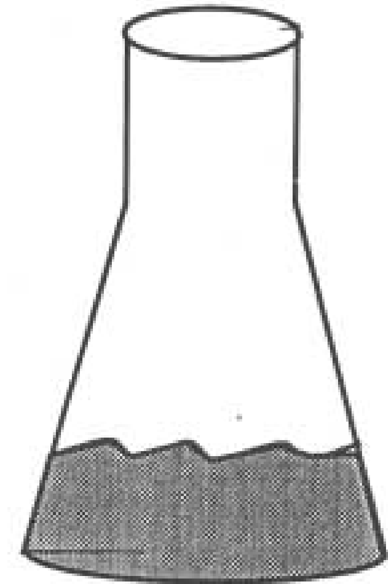
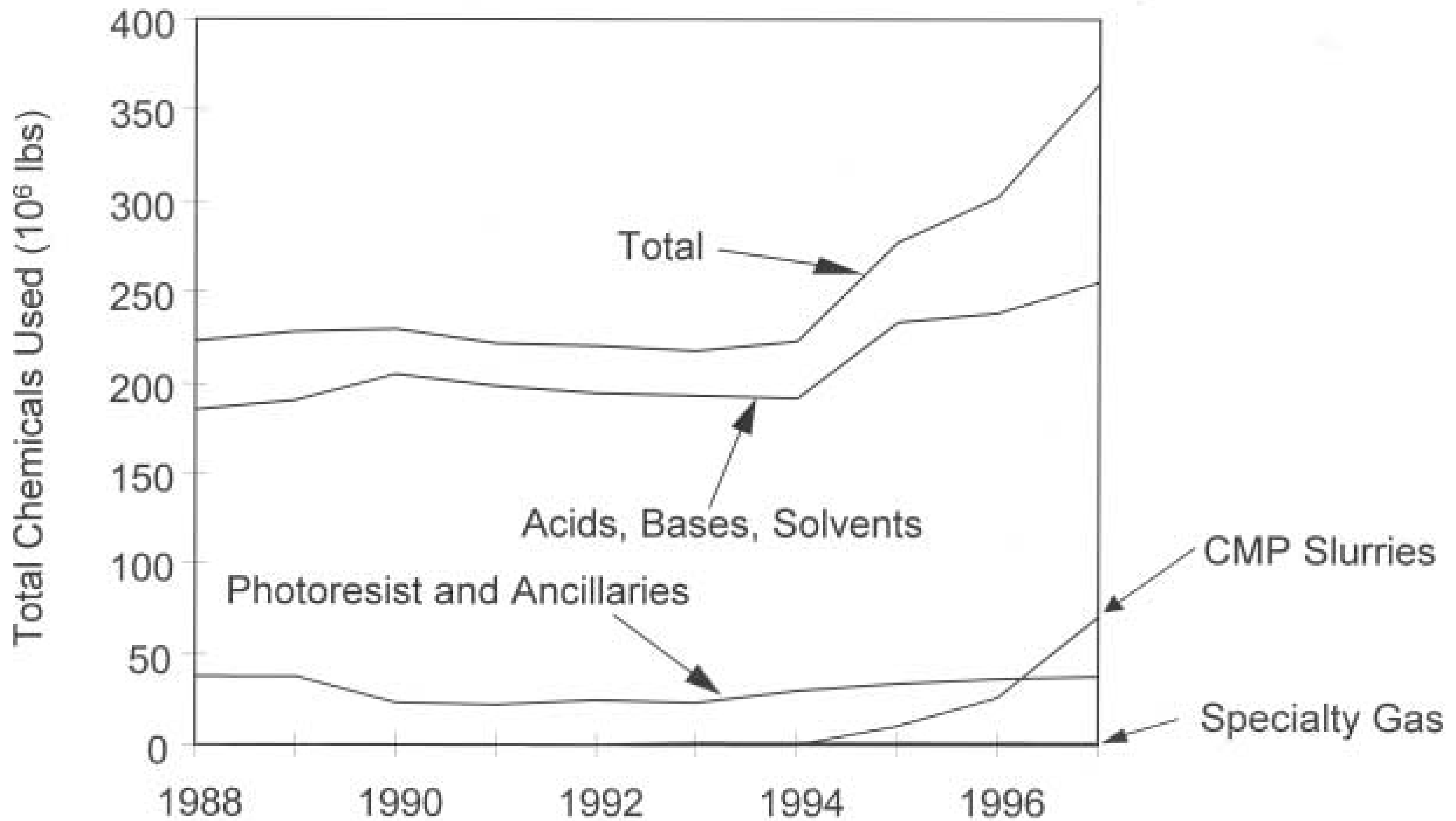
Conventional Dry Ashing







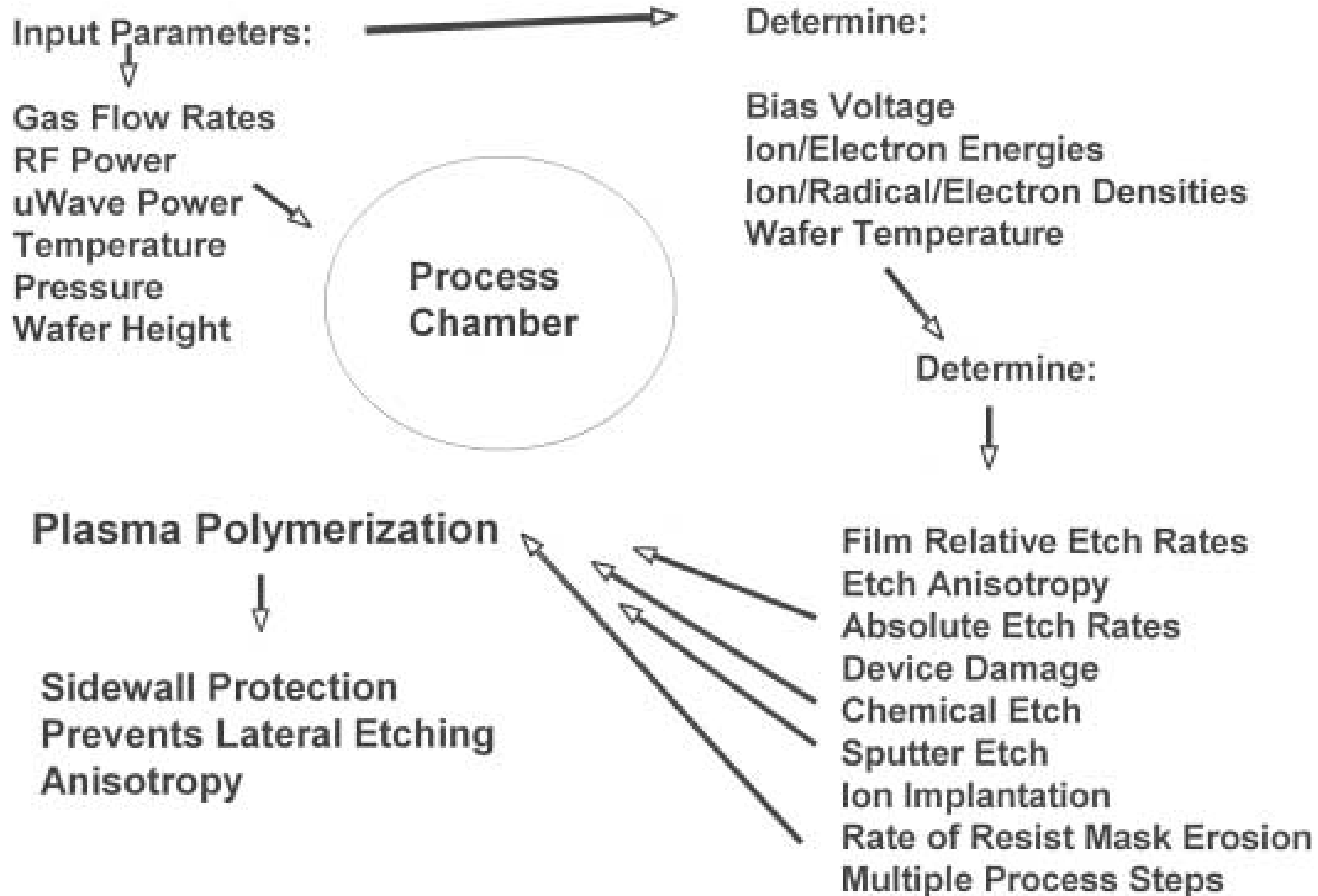
Total U.S. Chemical Usage



ULVAC's Solution: Solvent Free ENVIRO^{TM} Process

- **Multi-step low temperature plasma clean processes remove/solubilize etch polymer veil**
  - Low temperature process to avoid oxidizing metallic in the polymer veil
  - RIE to remove plasma modified/ damaged skin layer
  - Halogen μwave downstream chemistry to strip/solubilize bulk resist and etch polymer veil
- **NO corrosive solvent clean needed**
- **Highly selective to W, TiN, TiW, Ti and SiO_2**

Plasma Etching in a Nutshell…



Boiling Points of Typical Metal-Etch Products Entrained in Polymer

Fluoride	Units ºC	Chloride	Units ºC
WF_6	20	WCl_6	345
WOF_4	190	$WOCl_4$	230
MoF_6	35	$MoCl_5$	270
$MoOF_4$	180	$MoOCl_4$	180
TiF_4	285 s	$TiCl_4$	35
TaF_5	230	$TaCl_5$	240
SiF_4	-85	$SiCl_4$	60
AlF_3	1290 s	$AlCl_3$	180 s

Developing a Water Soluble ENVIRO^{TM} Process

- Diagnose carefully all of the process mechanisms taking place during the plasma etch. Note there is bulk resist to be ashed, sidewall polymer to be ashed and solubilized, possible insoluble material to be removed.
- Each step in the plasma etch process is critically important.
- Based upon this diagnosis, envision what and where the insoluble residues might be within the polymeric structure.

Developing a Water Soluble ENVIRO™ Process (Cont.)

- Plan out an ENVIRO™ process sequence which could treat layer-by layer of residue and result in a soluble residual final ash.
- Try the process on sample chips and inspect for cleanliness.
- Based on SEM inspection, modify the process as seems appropriate, run another sample, and examine again.
- Iterations are continued until a totally clean process is the result.

Enviro™ Processing in a Nutshell

Multiple Sequential In-situ Process Steps to Render All Polymer Etch-Residue Layers
(100% Soluble in DI Water)

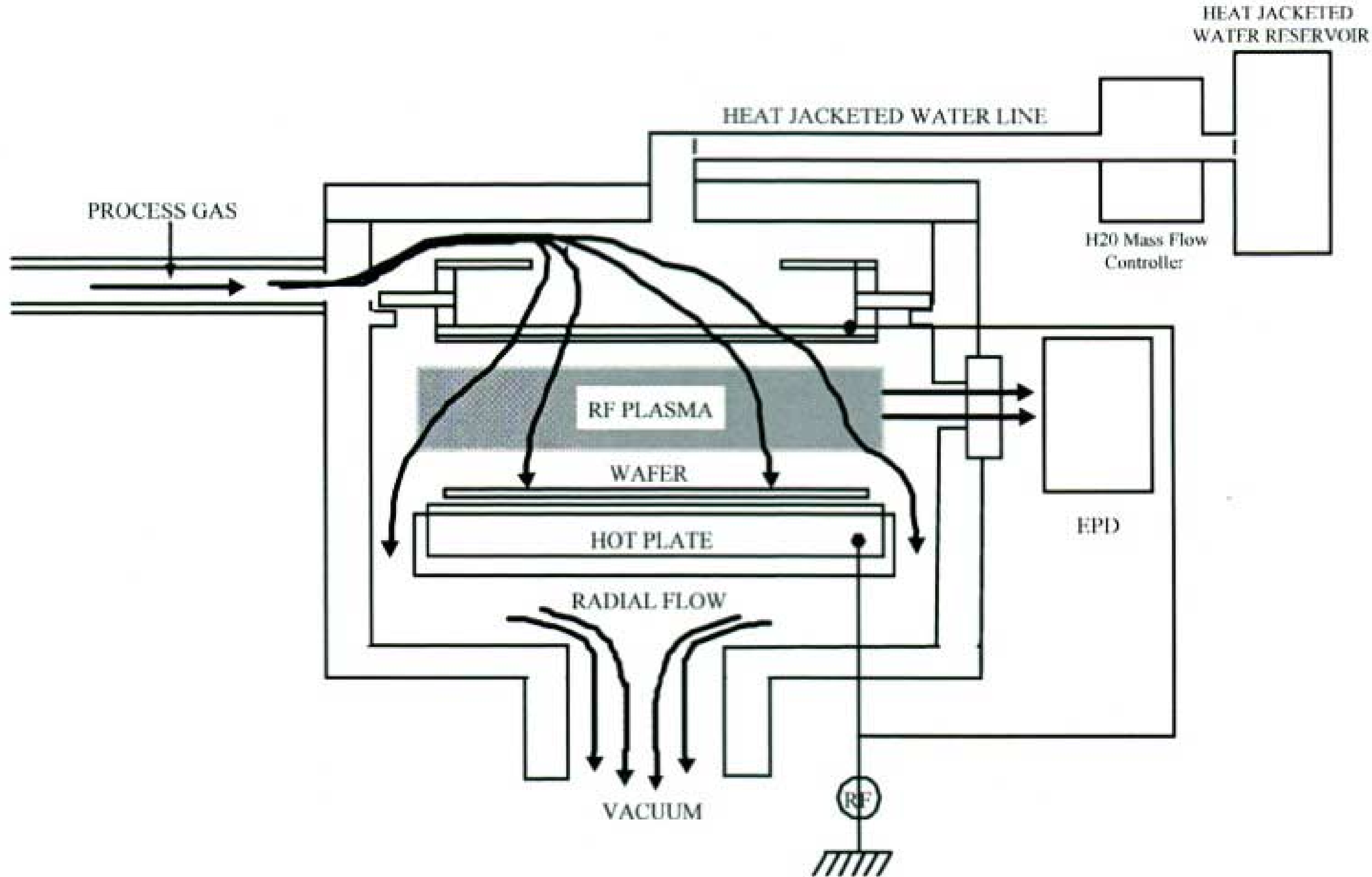
Parameters Available for Each Step:

- Gases: up to 6
- Pressure: 0.05-10 Torr
- RF Power: 0-650 Watts
- Uwave Power: 0-2000 Watts
- 100% Neutral Radical Processing

Enviro™ Processing in a Nutshell (cont.)

- 100% RIE Ion Processing
- Ion-assisted Radical Processing
- Temperature
- Time
- Bias Voltage
- Endpoint Mode
- Wafer Elevation

Reactive Ion Stripping Chamber



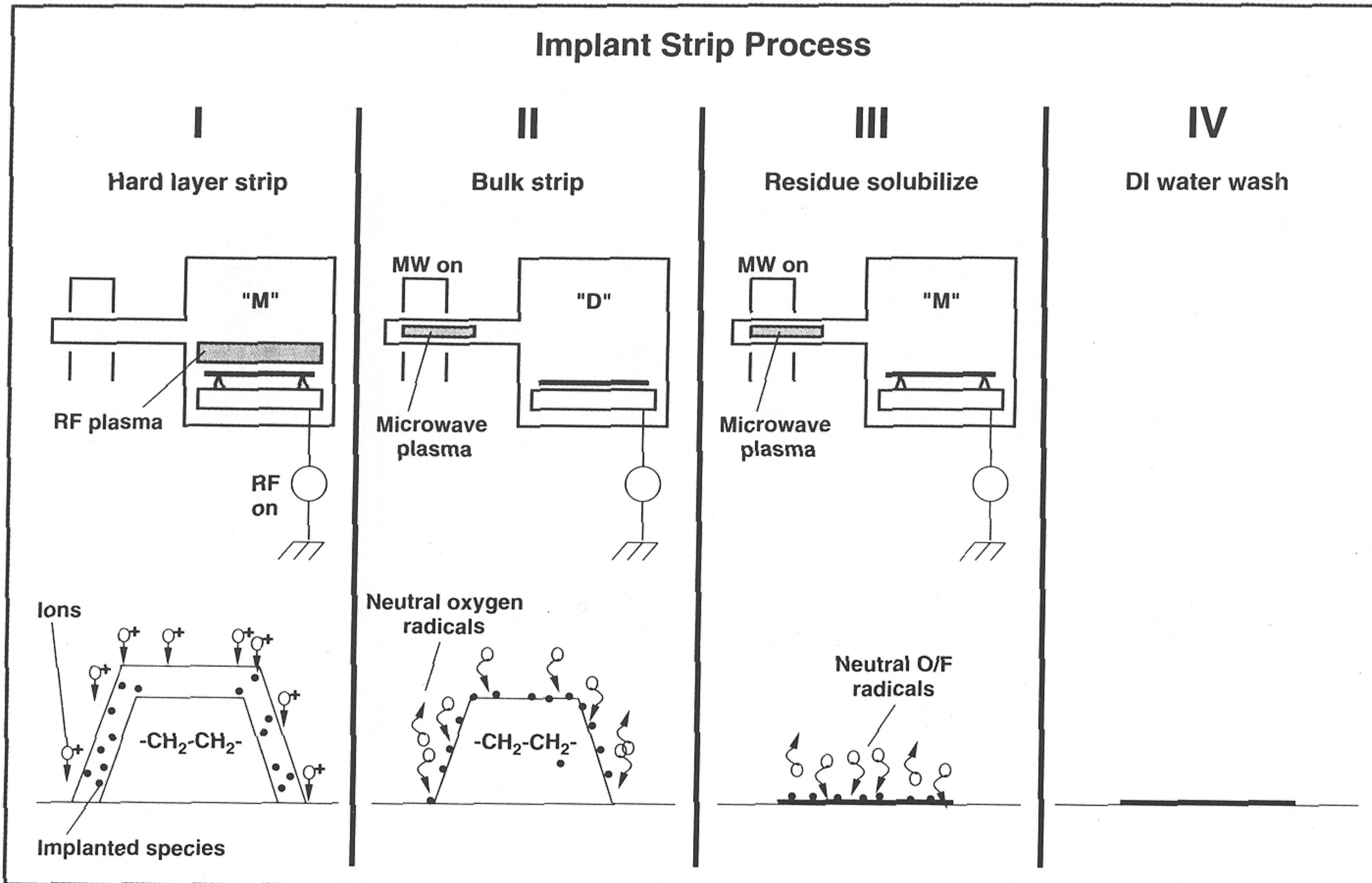
P+ IE16 100KeV Implant

Bubbles in Resist 80ºC   Blister Formation 120ºC

Burst Blisters 140ºC   Bare Silicon Spot 140ºC

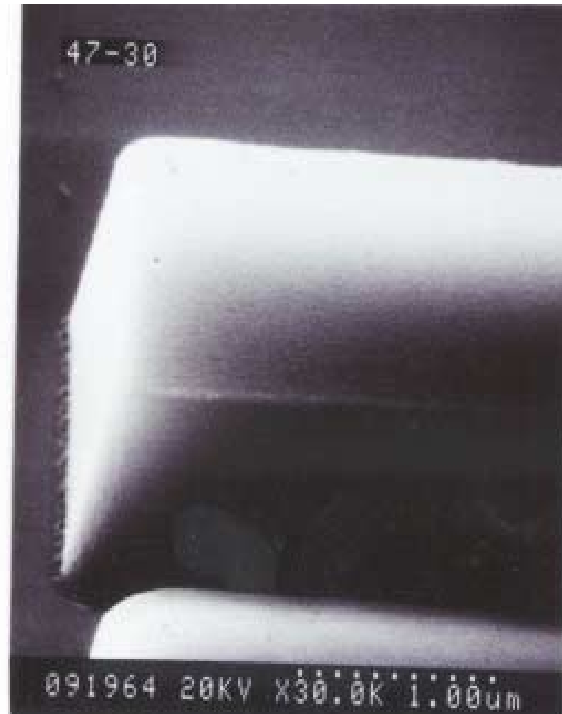
The "Hard" Layer

Popped Resist


Implant Strip Process
I
Hard layer strip
"M"
RF plasma
RF
on
Ions
-CH2-CH2-
Implanted species
II
Bulk strip
MW on
"D"
Microwave
plasma
Neutral oxygen
radicals
-CH2-CH2-
III
Residue solubilize
MW on
"M"
Microwave
plasma
Neutral O/F
radicals
IV
DI water wash

5E15 As 80KeV Implant

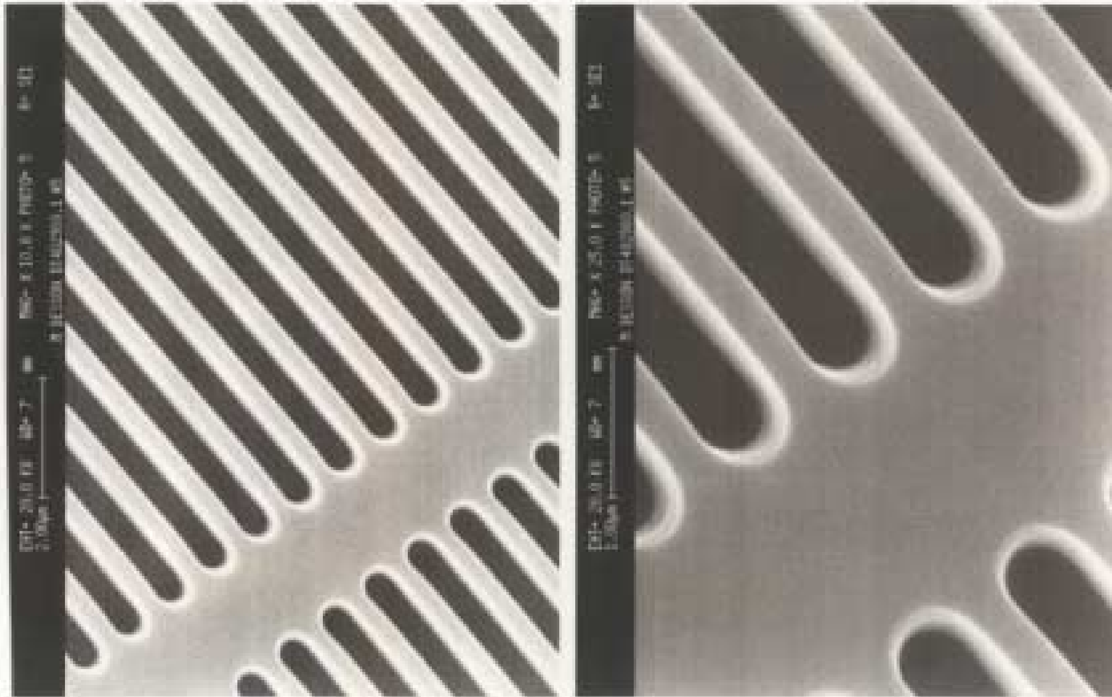
O_2 RIE 20 Seconds



O_2 RIE 30 Seconds

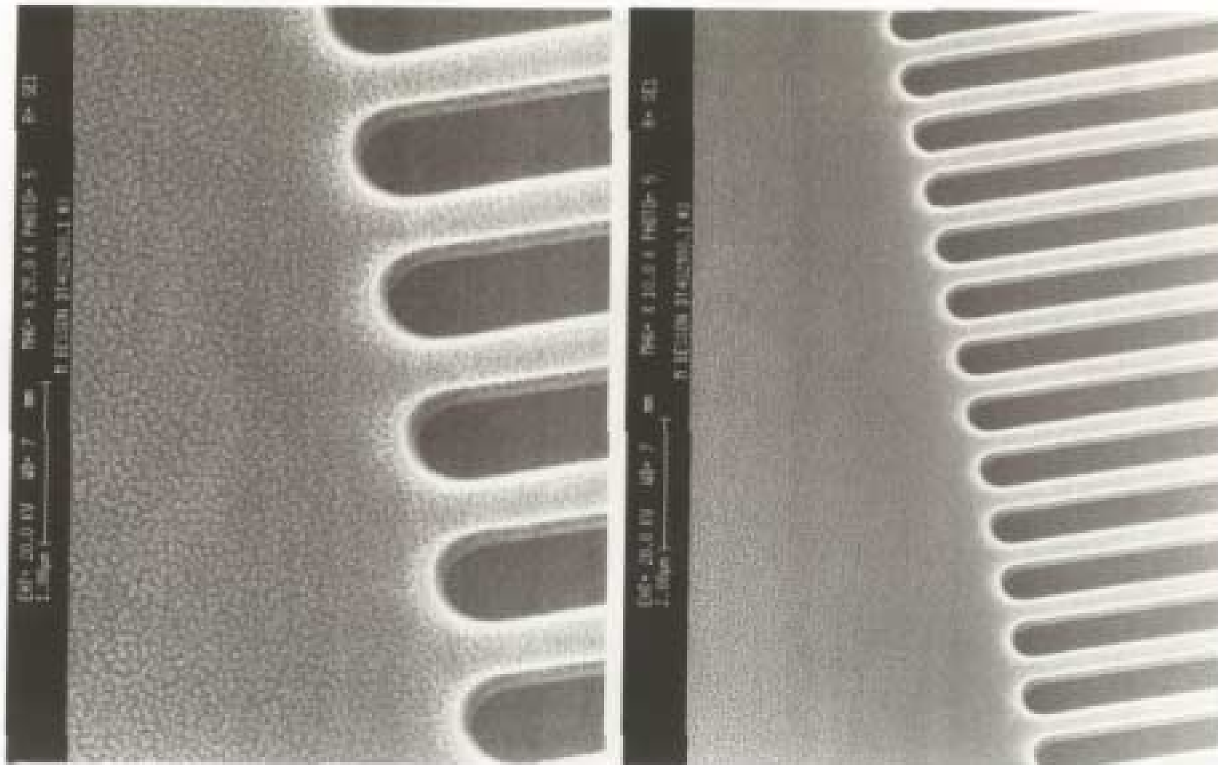
O_2 RIE 60 Seconds

ENVIRO™ Processed 1E16, 120KeV As High Dose Implant



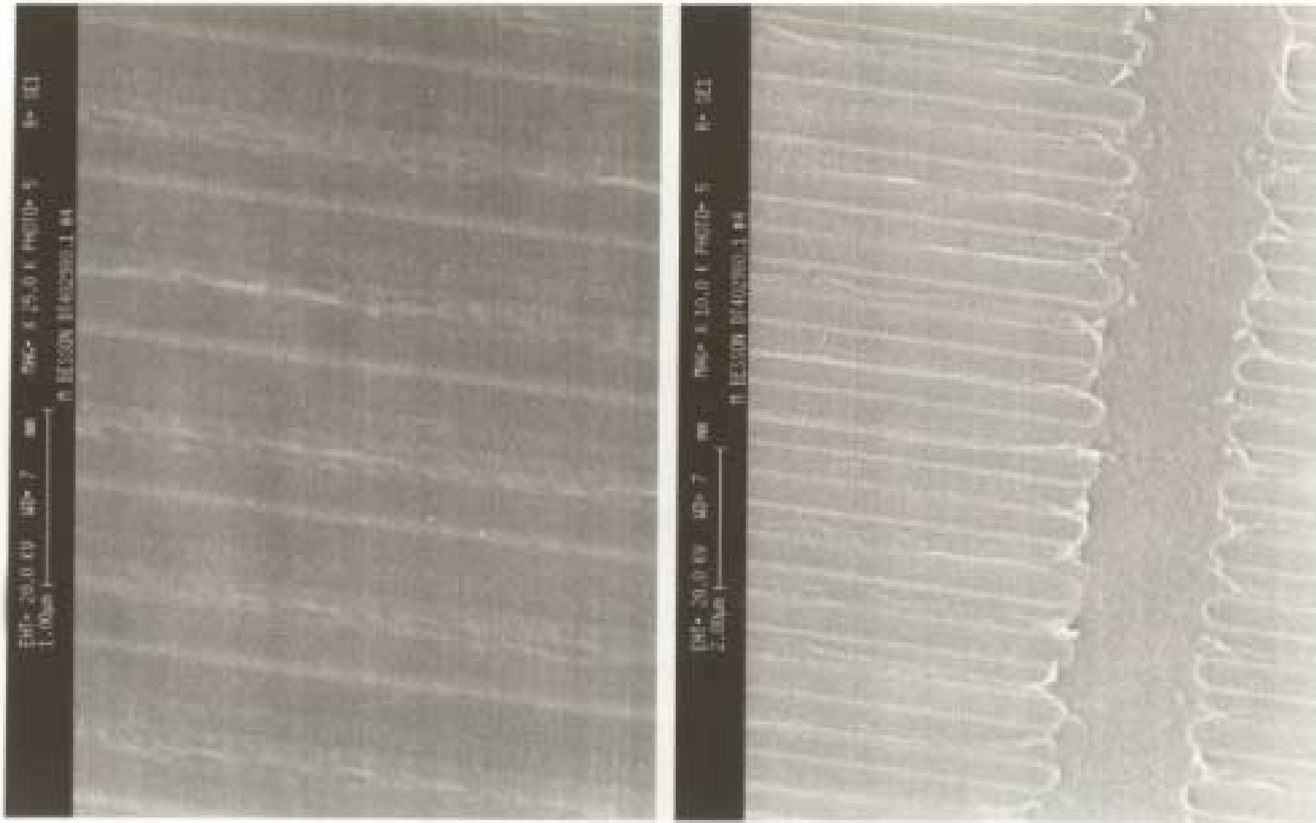
Reference Before Process

ENVIRO™ Processed 1E16, 120KeV As High Dose Implant (1)



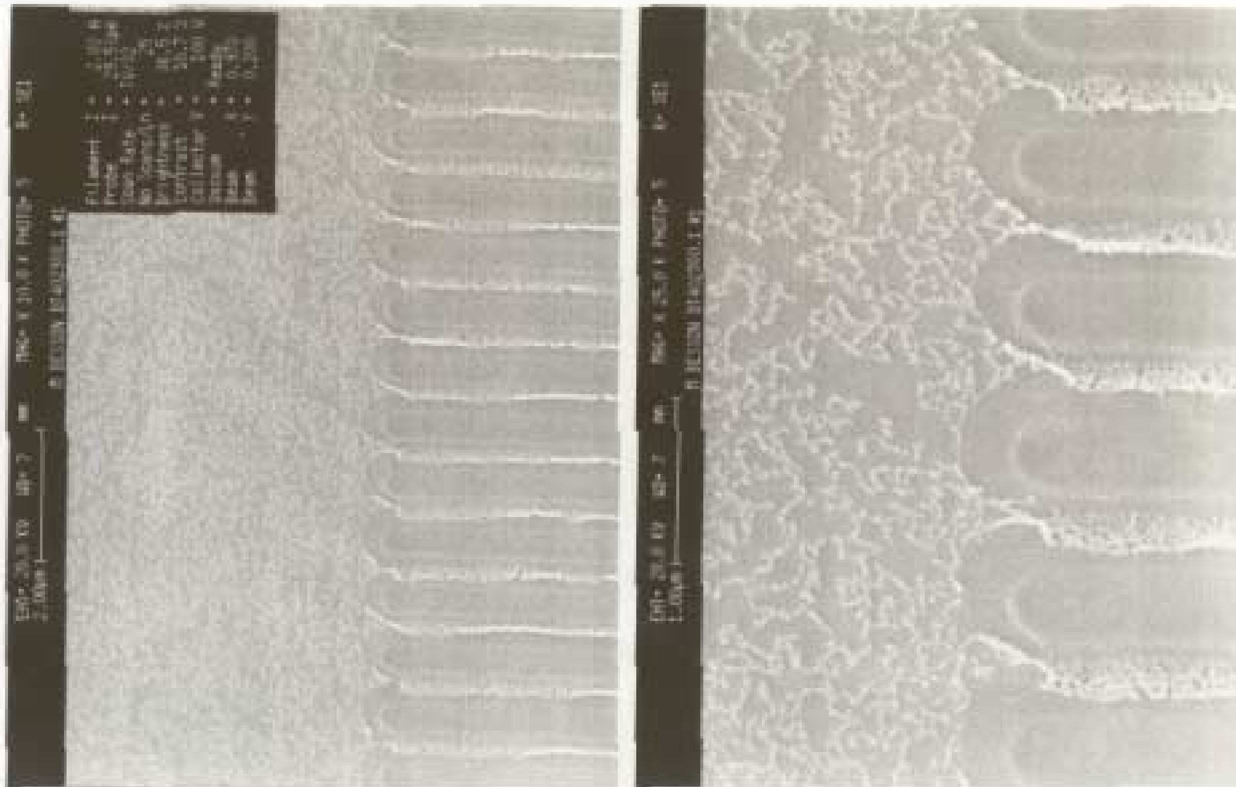
Step 1: O_2 RIE Strip

ENVIRO™ Processed 1E16, 120KeV As High Dose Implant (2)



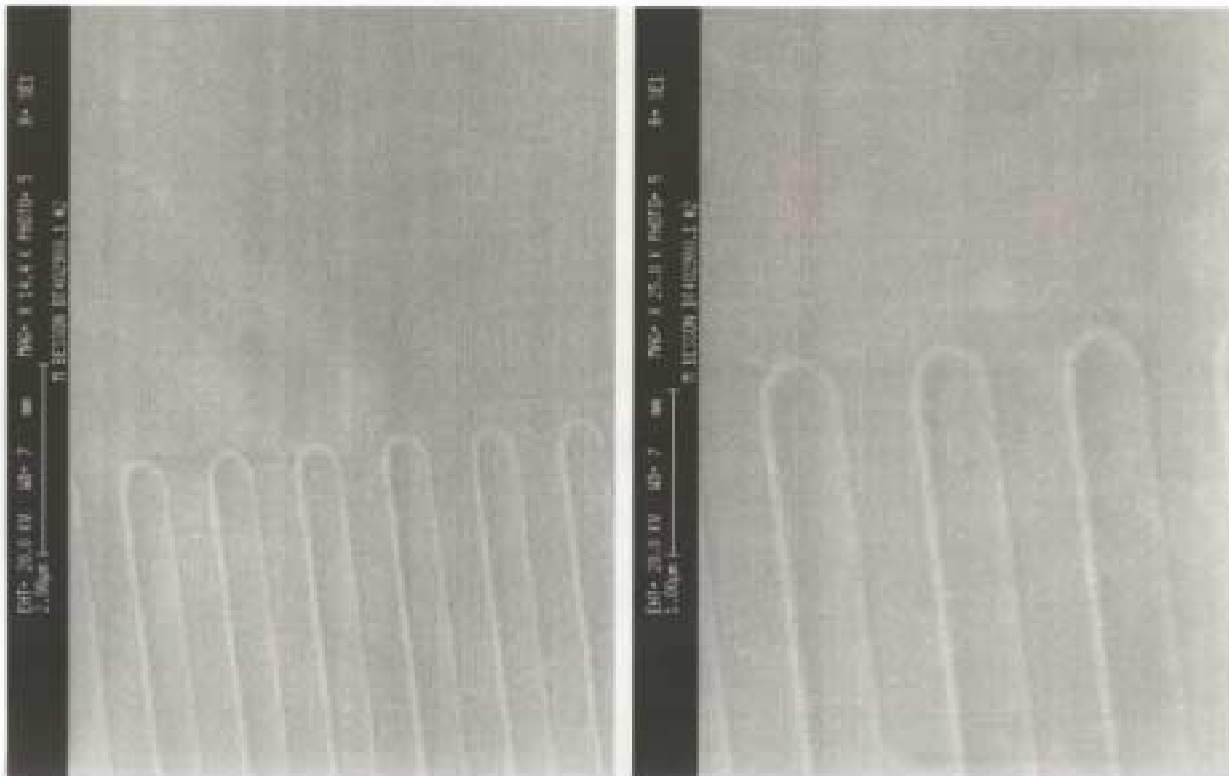
Step 2: Remote Microwave Plasma Strip

ENVIRO™ Processed 1E16, 120KeV As High Dose Implant (3)



Step 3: Remote Microwave Plasma Solubilization

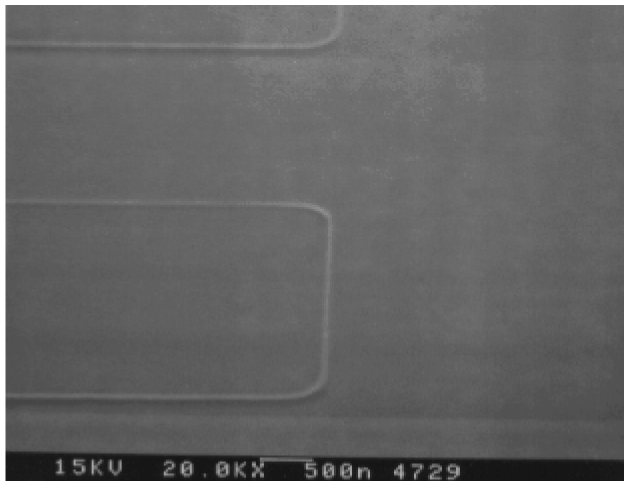
ENVIRO™ Processed 1E16, 120KeV As High Dose Implant (4)



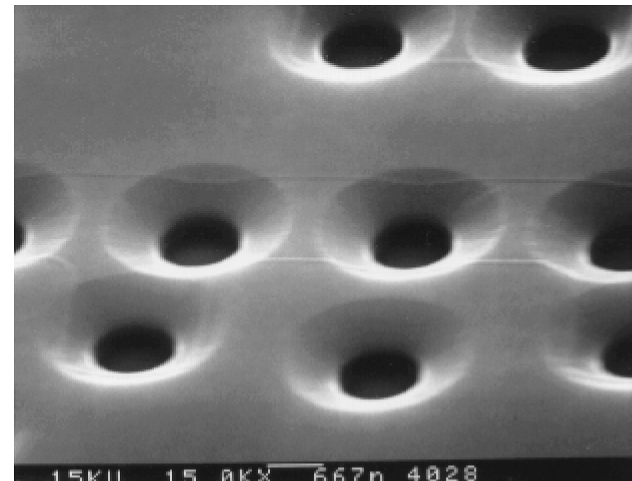
Step 4: DI Water Rinse

Examples for Post High Dose Implant Strip & Clean

As^+, 1.5E16



P^+, 1E16, No Bake



Critical BEOL Processes

METAL AND VIA

ETCH METAL

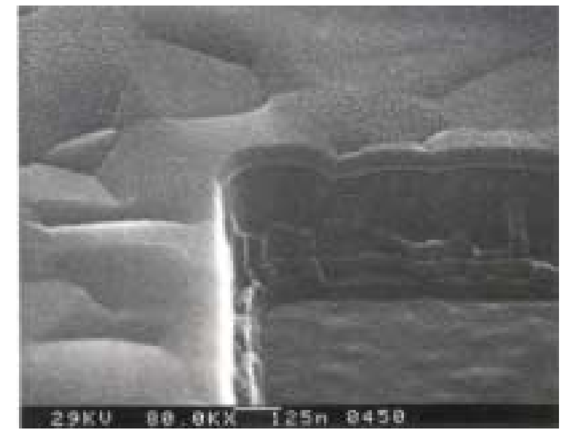
DEPOSIT METAL
APPLY PHOTORESIST
PATTERN PHOTORESIST
ETCH METAL
STRIP PHOTORESIST
CLEAN WAFER

ETCH VIA

DEPOSIT OXIDE [TEOS]
APPLY PHOTORESIST
PATTERN PHOTORESIST
ETCH VIAS
STRIP PHOTORESIST
CLEAN WAFER

3 TIMES OR MORE

TiN / AlCu / TiN



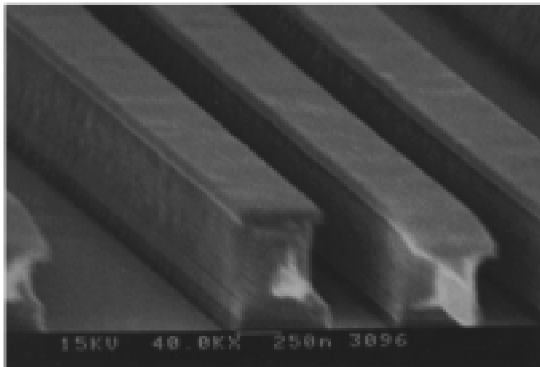
Post Etch

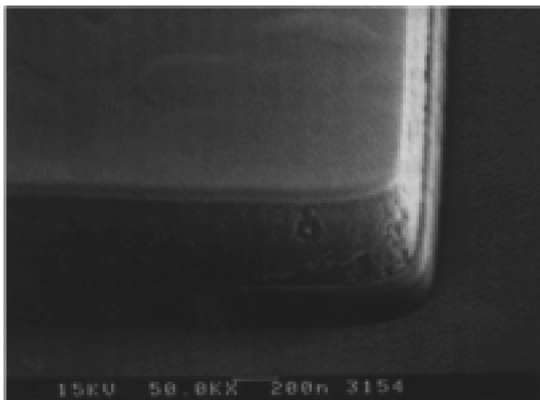
Post Strip
Pre Di Rinse

Post DI Rinse

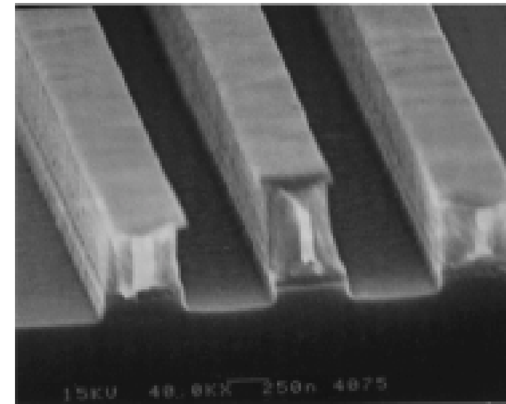
Metal Lines Are Free of Polymer Residue After Solvent Free ENVIRO™ Clean & DI Rinse

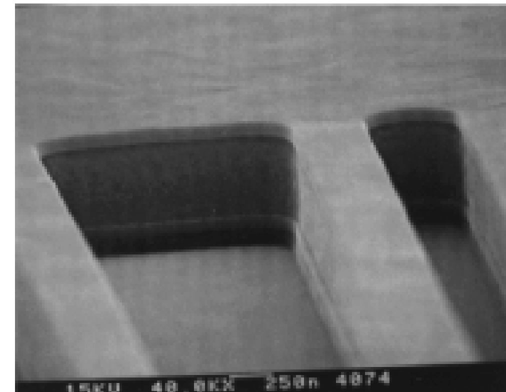
Metal 1



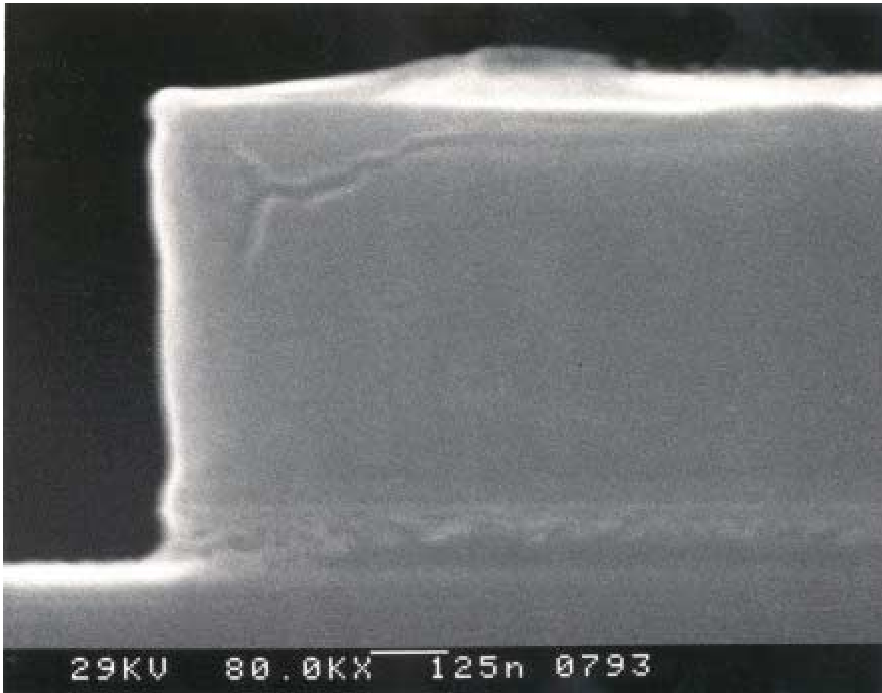


Metal 2

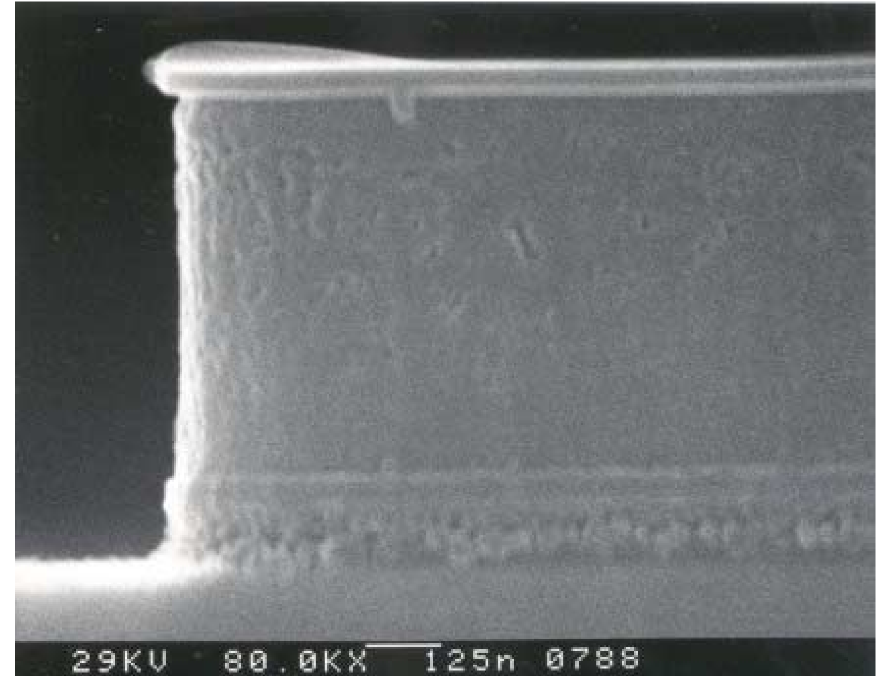




TiN / AlCu / TiN

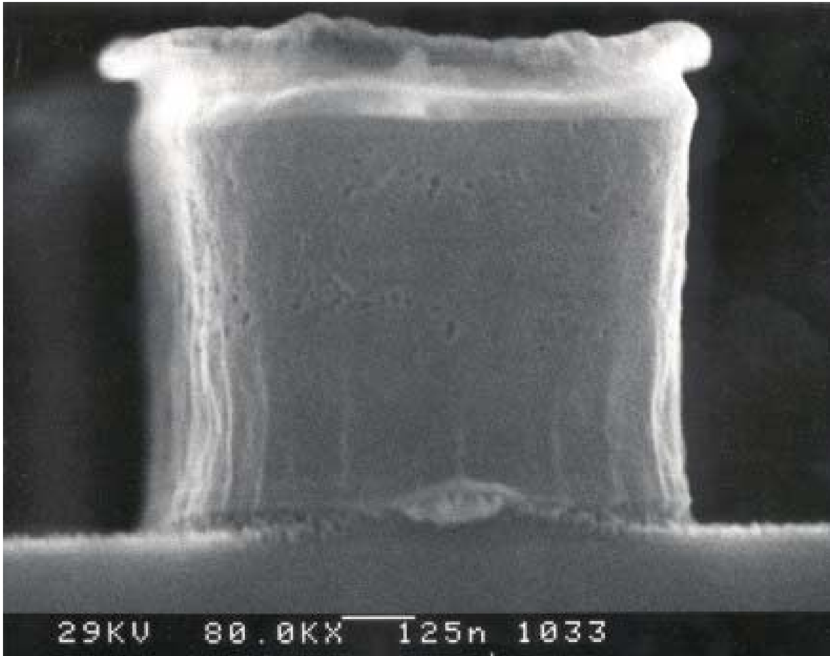


Post Strip
Pre DI Rinse

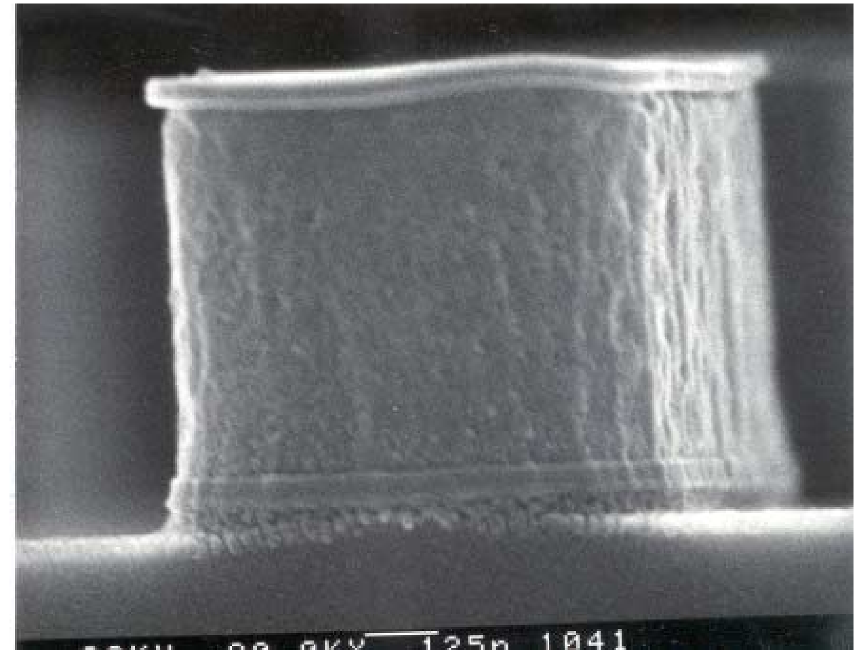


Post DI Rinse

TiN / AlCu / Tin After Process

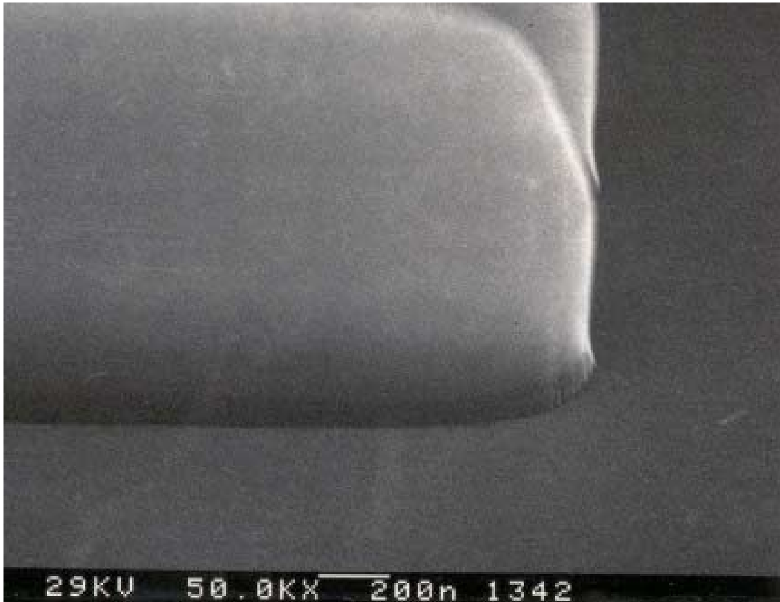


Pre DI Rinse

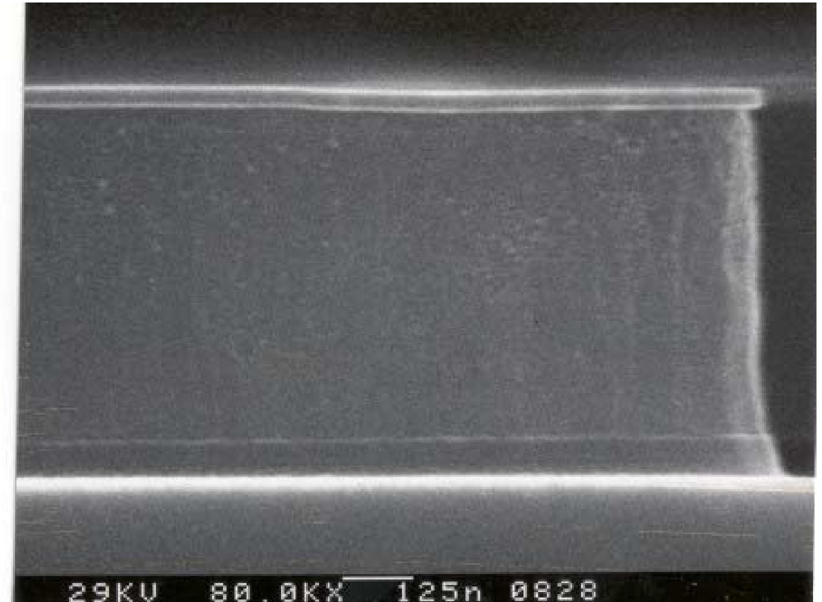


Post DI Rinse

TiN / AlCu / TiN

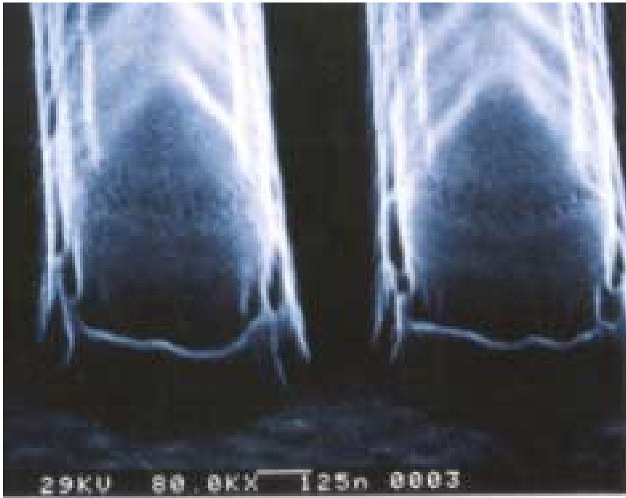


Reference Before Process



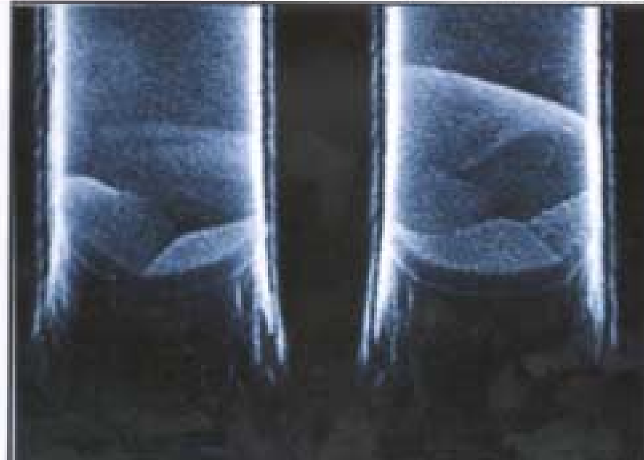
Post Enviro™ Process

Post Metal Etch



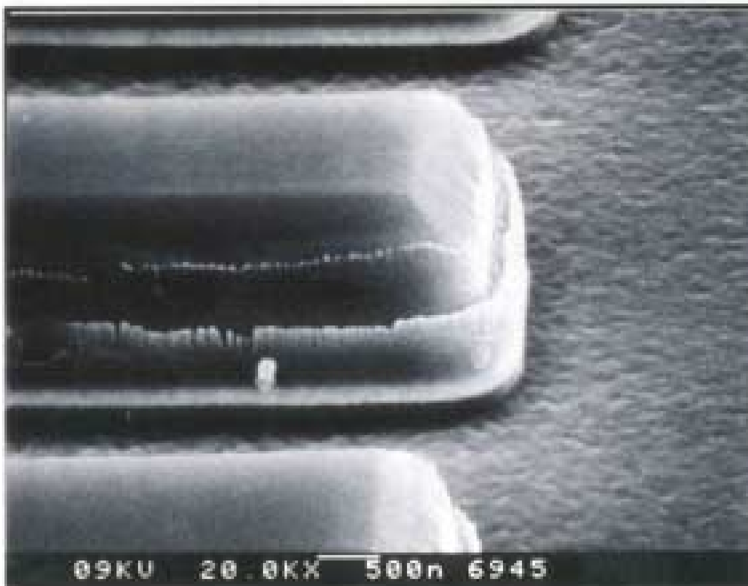
PRE-STRIP

POST-STRIP
PRE-WASH

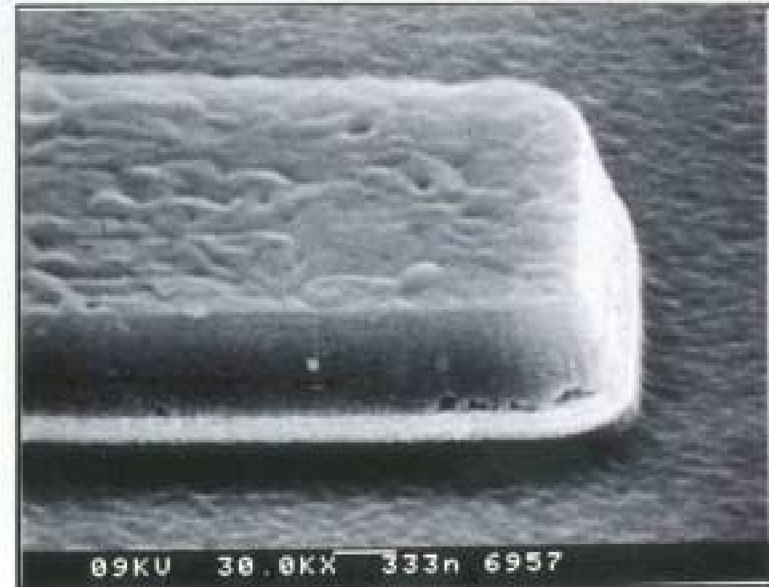


POST-STRIP
DI WATER RINSE/DRY

Al-Si-Cu (4%) TiW
Etch Process: BCl_3, Cl_2, CHF_3, SF_6

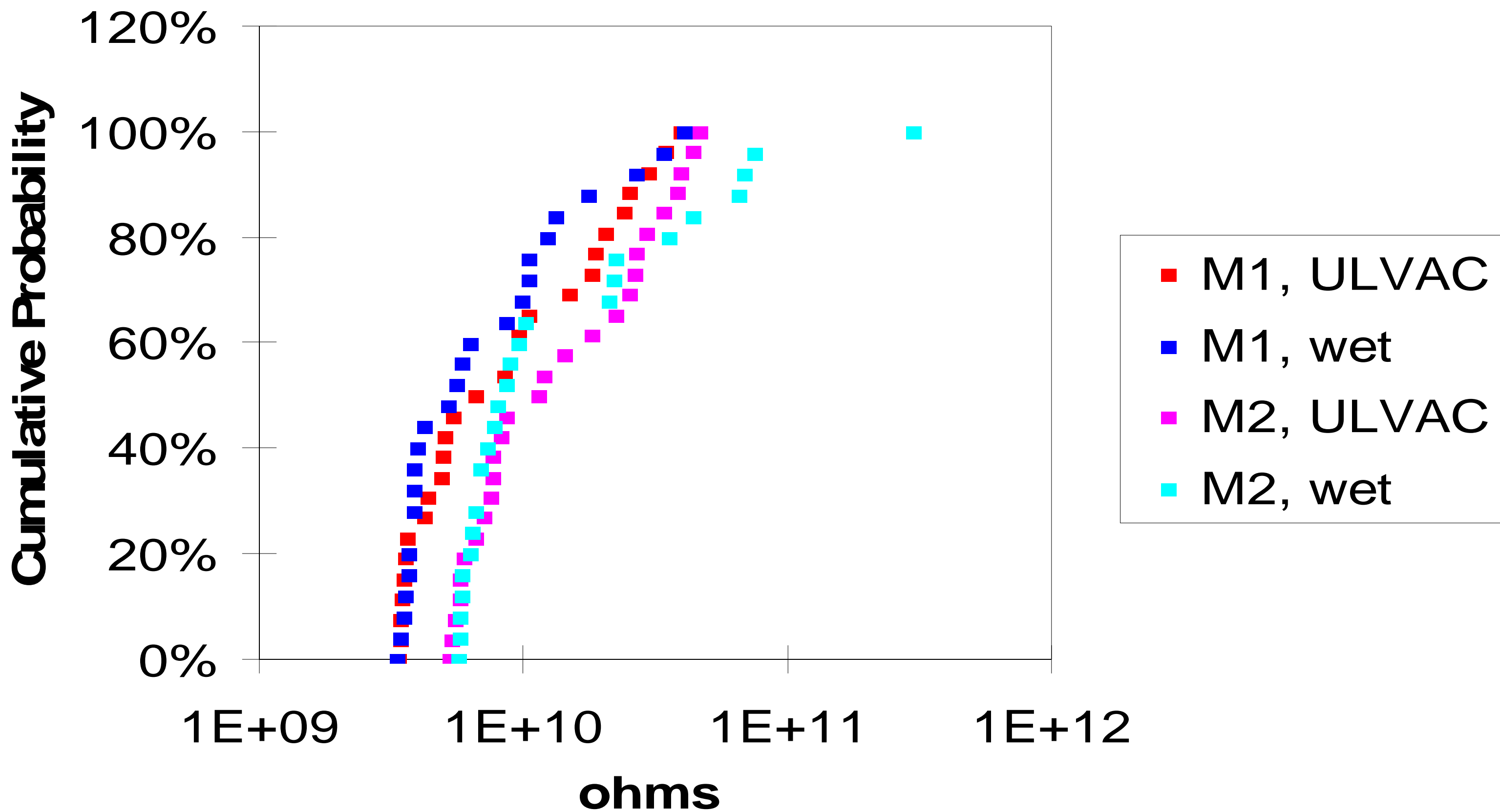


POST-ETCH
PRE-STRIP

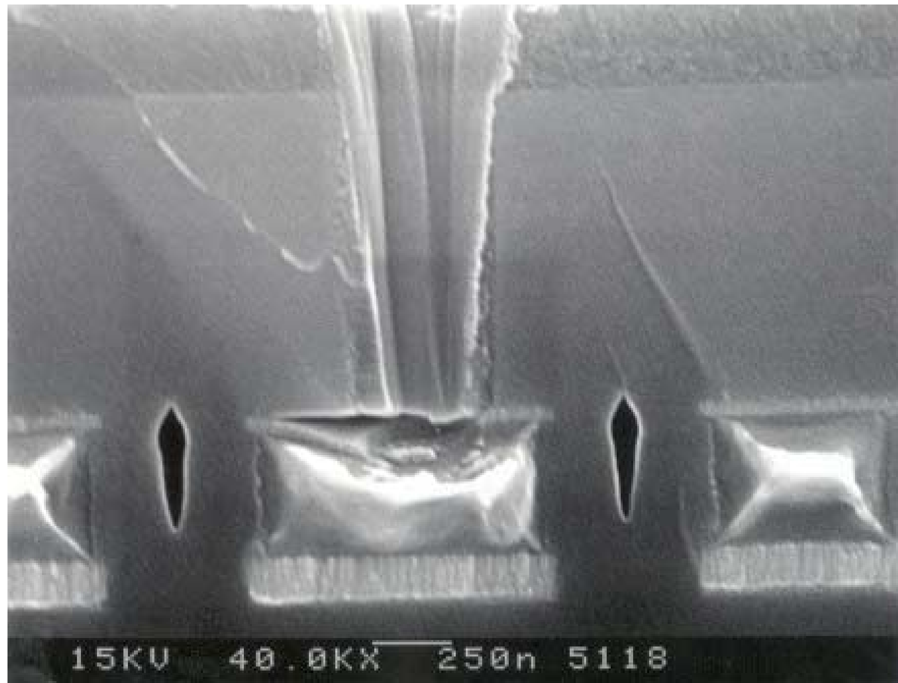


POST-STRIP
DI WATER RINSE/DRY

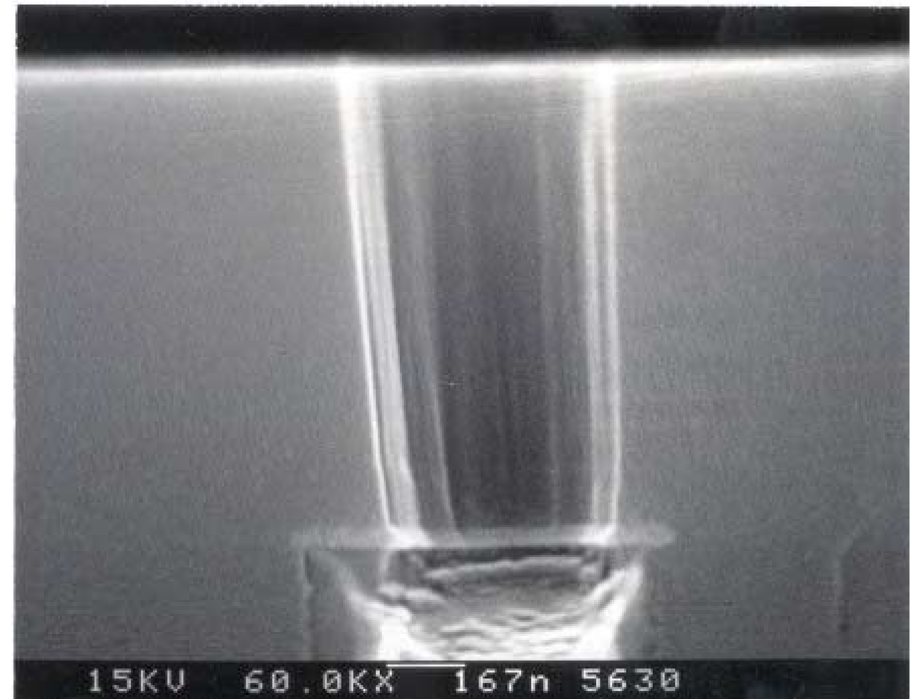
Metal Line Bridging Resistance of Solvent Free ENVIRO™ Process same as Wet Clean



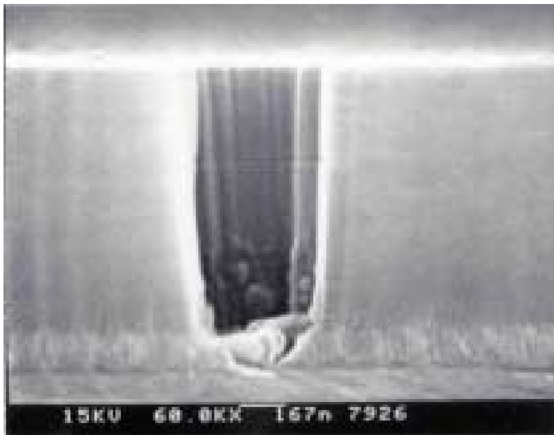
After Dry Etch

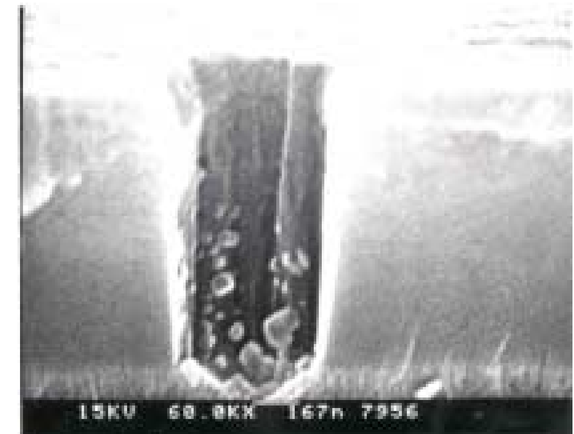


ENVIRO™ Process with DI Rinse

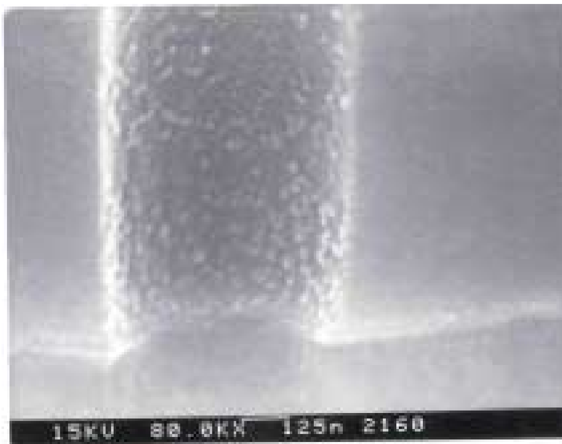


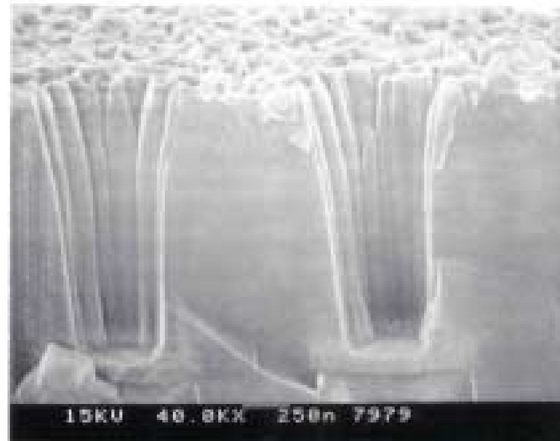
ENVIRO™ Dry Residues Before DI Rinse



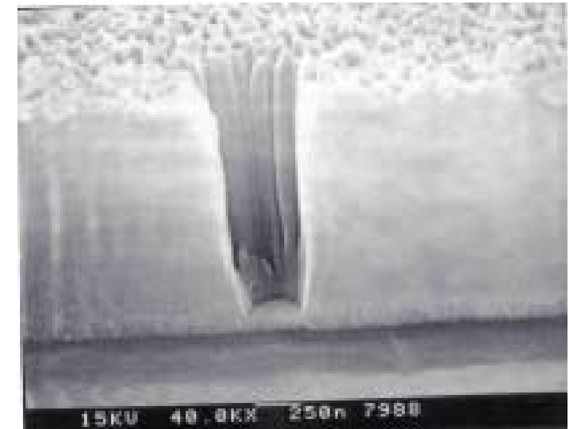


ENVIRO™ Dry Residues Before DI Rinse





Before Enviro™

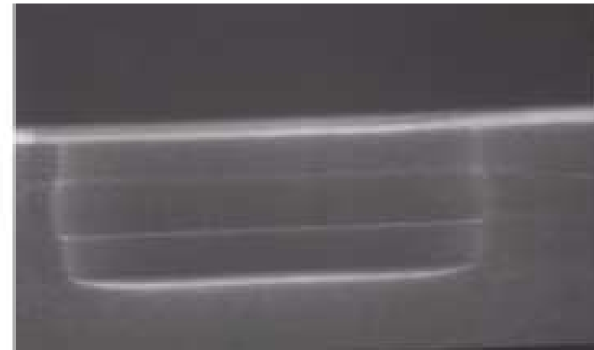


Before Enviro™

Low Pressure RIE for Organic SOG Via Stripping

- Conventional Dry ashing: SOG damage, via poisoning
- ENVIRO™ low pressure RIE ashing: no SOG damage
- Applicable to some low-k spin on polymers

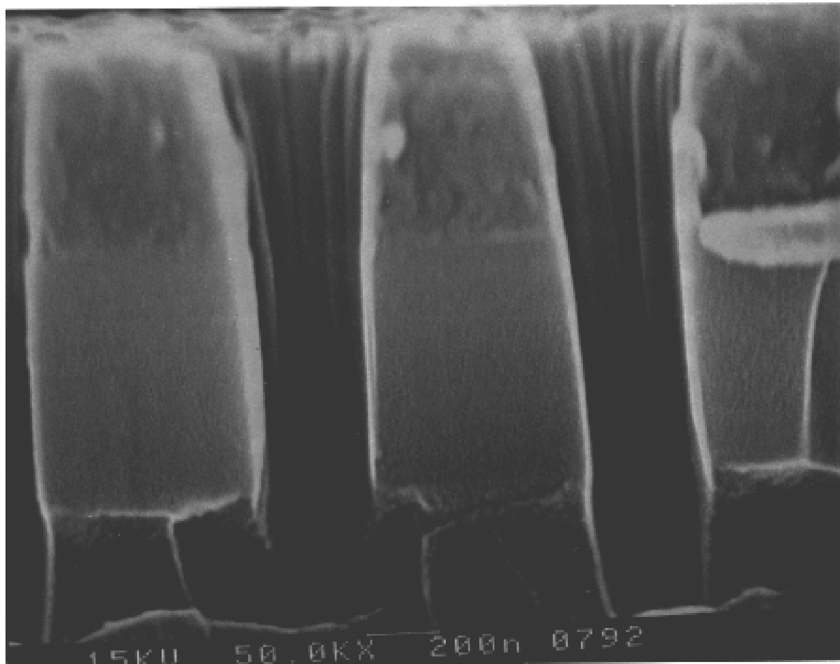
Conventional



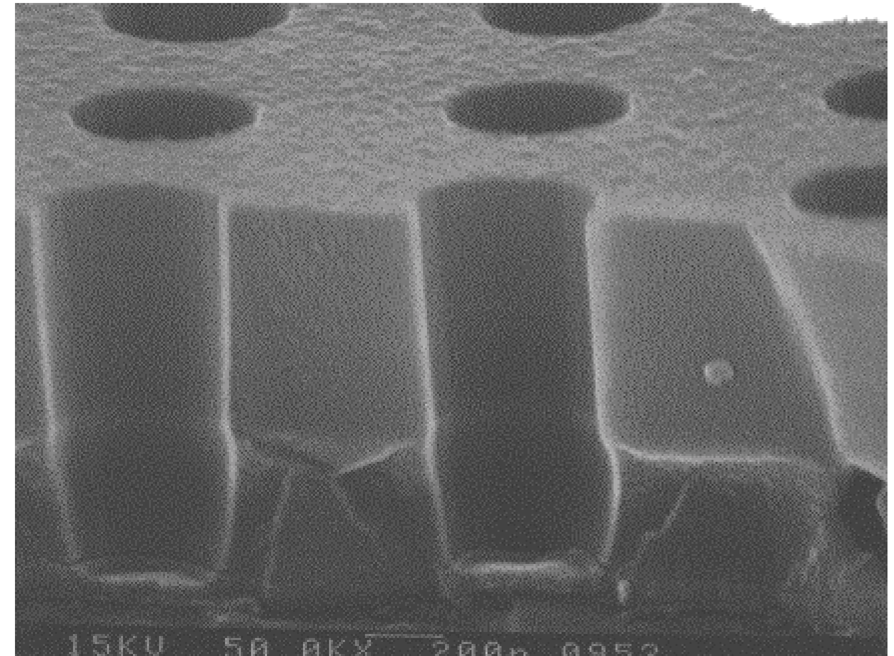
ENVIRO™

Resist & Etch Sidewall Polymer Strip After HSQ Via Etch

Filmstack: I-line Resist /USG / HSQ



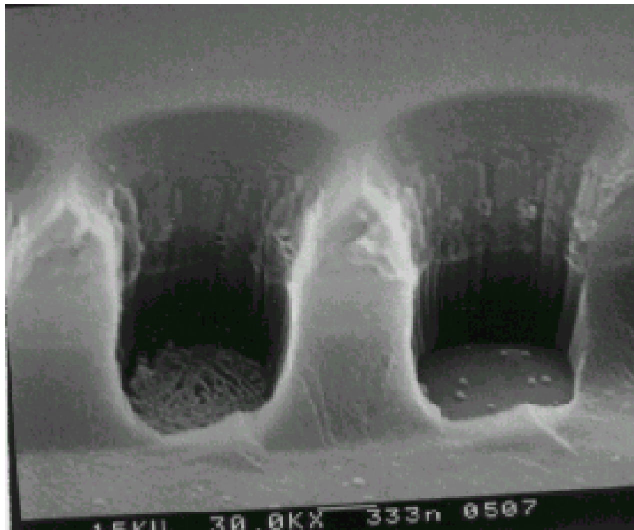
Before ENVIRO^{TM} strip process

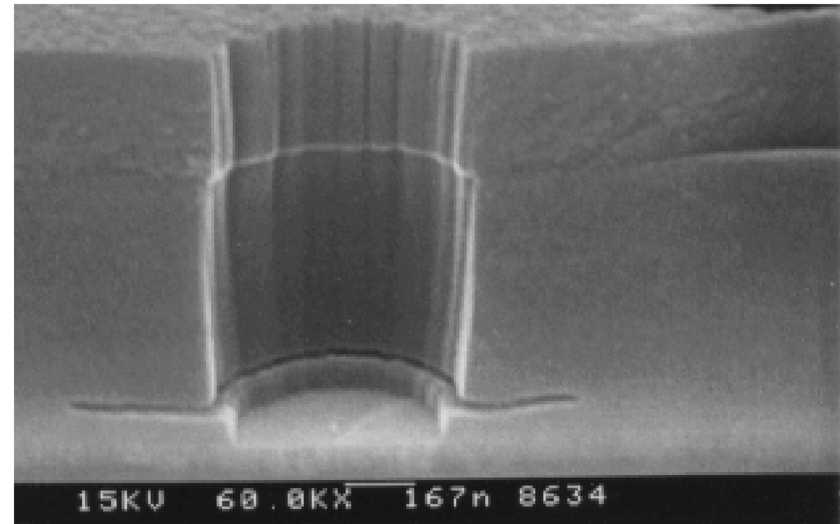


After ENVIRO^{TM} strip process

Resist & Etch Sidewall Polymer Strip After Low-k Via Etch

Filmstack: I-line Resist / SiO_2 / CVD Methylsilane Oxide

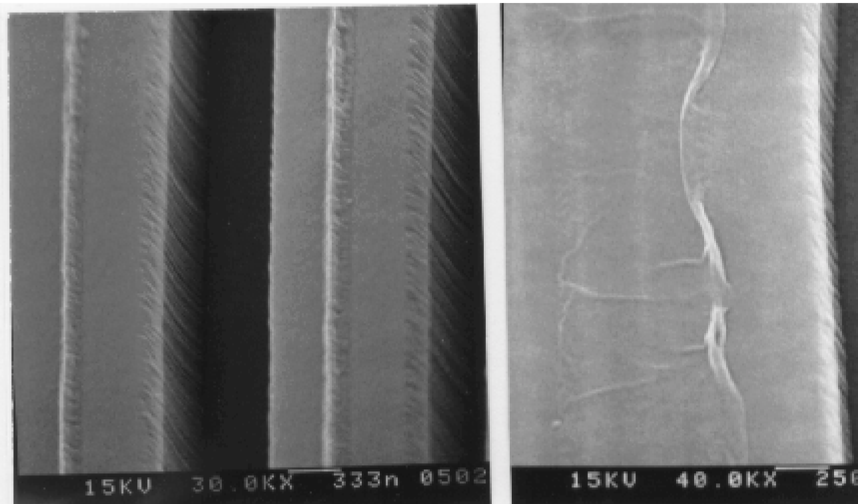




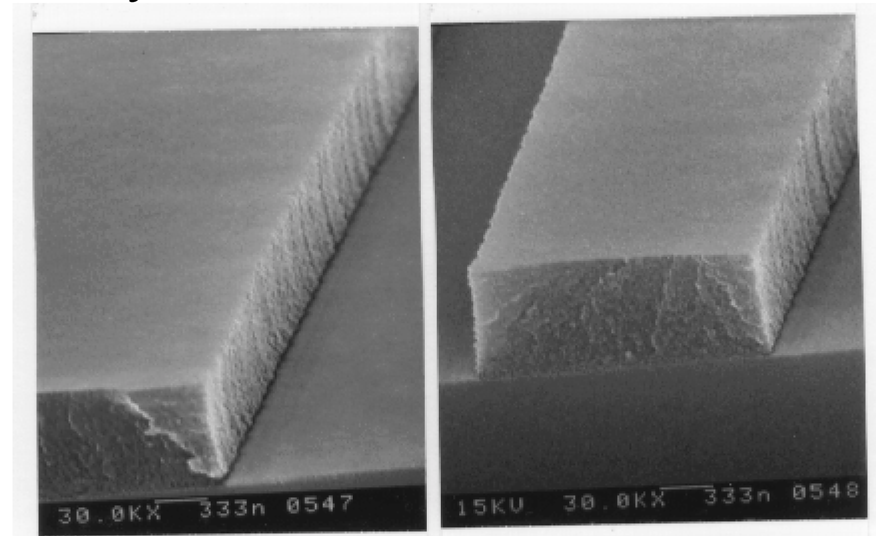
Before ENVIRO™ Strip process   After ENVIRO™ strip process

Residue Clean After Fluorinated Polyimide Etch

Filmstack: 2000A SiO_2
6500A Fluorinated Polyimide



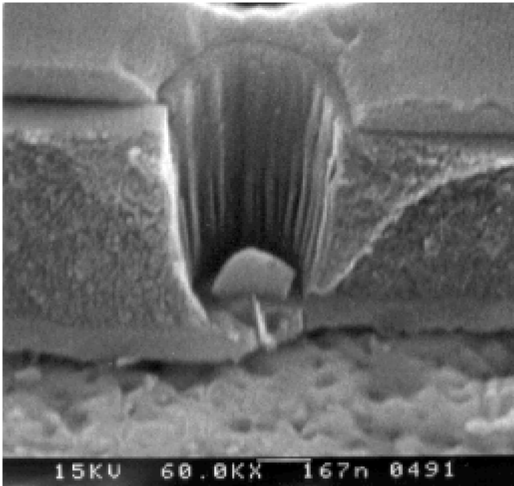
Before ENVIRO™ clean process



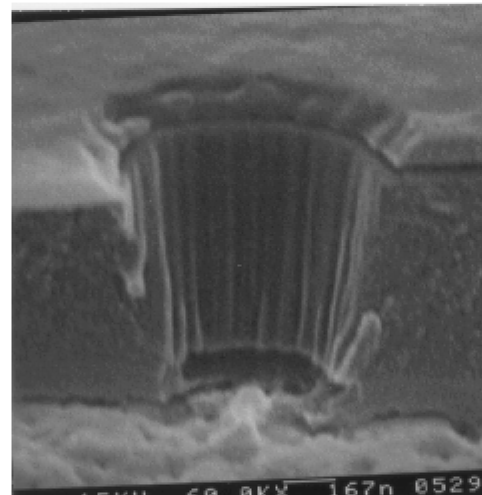
After ENVIRO™ clean process

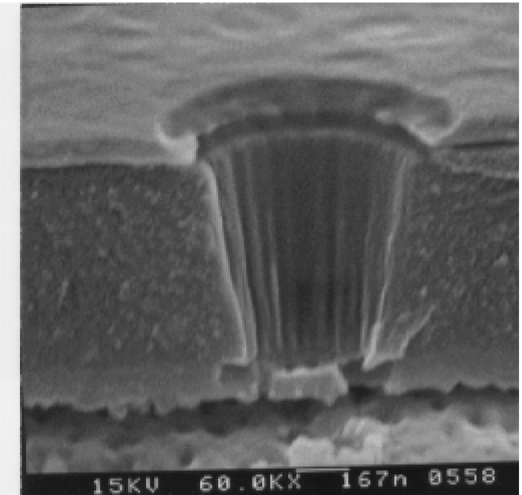
Residue Clean After SiLK Via Etch (to Cu)

Filmstack: 1000A SiO_2
7000A SiLK
1000A Si_3N_4
15000A Cu



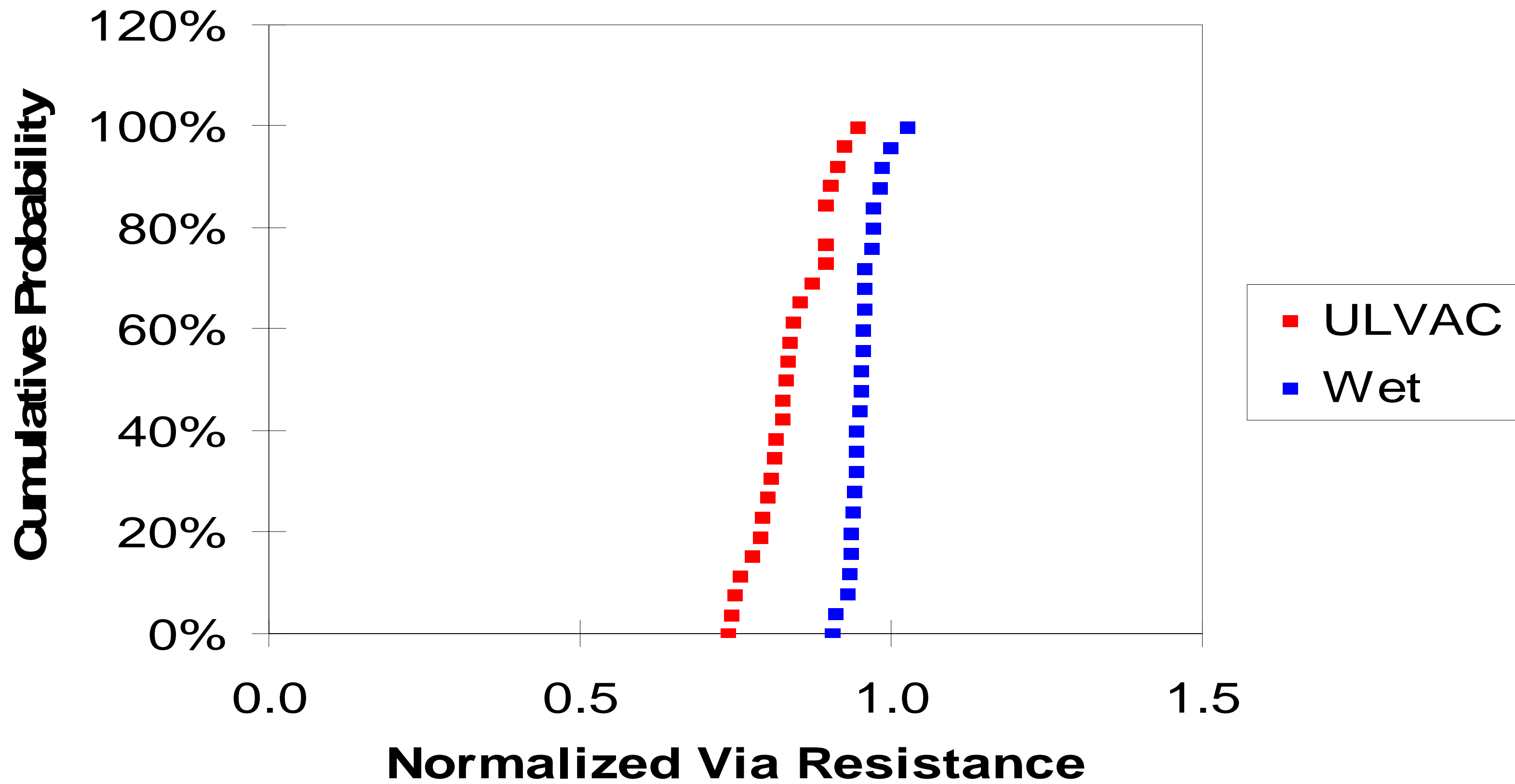
Before ENVIRO™ clean process





After ENVIRO™ clean process

Via Contact Resistance of ENVIRO™ Process Is Better than POR (Wet Clean)



SUSTAINABILITY OF CONVENTIONAL ASHING

A. 520,000 Wafer Starts/Year, 8 inch wafers
B. 1,040,000 Wafers Processed with 2 Metal Layers
C. Resist thickness after etching: ~1 micron, ~10E(-4) cm.
D. Resist Volume: 0.0314 cc of resist
E. @1gm/cm3 density, 31.4 milligrams of resist per wafer.
F. 1,040,000 wafers=71.8 pounds of resist stripped/year.
G. Assume 1% residue by weight(very high estimate)
H. Then 0.718 pounds of residue removed in one year.
I. HA usage: 41,614 Gallons/year
J. **This is~166,456 liters; @1 gm/cm3 density, this comes to 366,203 pounds of solvent to remove 0.718 pounds of residue!**
K. **312,109 Gallons of Isopropyl is used to rinse the solvent!**
L. **This is 2,746,559 pounds of rinser to remove solvent**.
M. **394,134 Gallons (3,467,334 Lbs) of non recoverable DI Water also used.**
N. This means 6,580,096 pounds of chemicals are consumed to remove 0.718 pounds of residue!!

Isn't there something wrong here?

THE ENVIRO PROCESS DOES THE SAME THING WITH 2,779,920 POUNDS OF RECOVERABLE DI WATER 3,376 pounds of O_2, 719 Pounds of NF_3, and 123 Pounds of H_2N_2