Gas phase surface preparation using ultraviolet-activated chlorine

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Outline

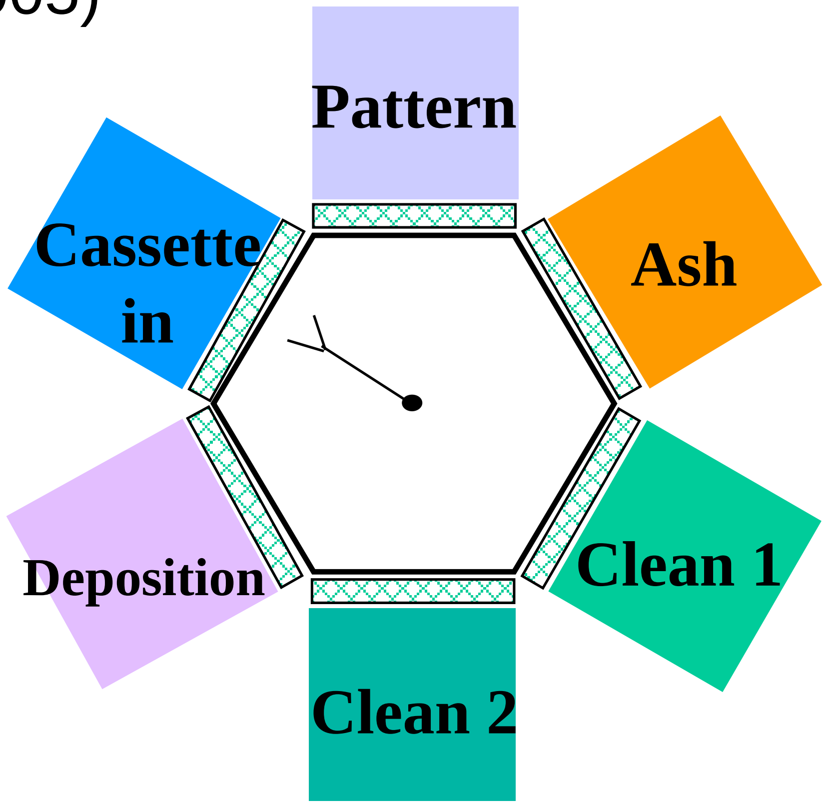
- Motivation for Gas Phase Surface Preparation
  - Processing
  - Environmental Safety and Health (ESH)
- Background Information: UV/Cl_2
- Experimental Setup and Preliminary Results
- Future Plans
- Summary

Front End Cleaning Steps

Contaminant	Application	Liquid Phase	Gas Phase
Organics	• Post-RIE • Ion Implant • Rework	• O_2 Ash • SPM (Piranha) • Ozonated Water	• UV-O_3 • UV-Cl_2 • Moist O_3
Oxide	• Pre-gate	• Dilute HF	• HF/vapor
Particles	• Post-CMP	• APM (SC-1) + megasonics • APM (SC-1) + brush scrubbing	• Cryogenic Aerosol • Laser
Metals	• Post-RIE	• HPM (SC-2) + chelating agents	• UV-O_3 • UV-Cl_2

Motivation — Gas Phase Cleans

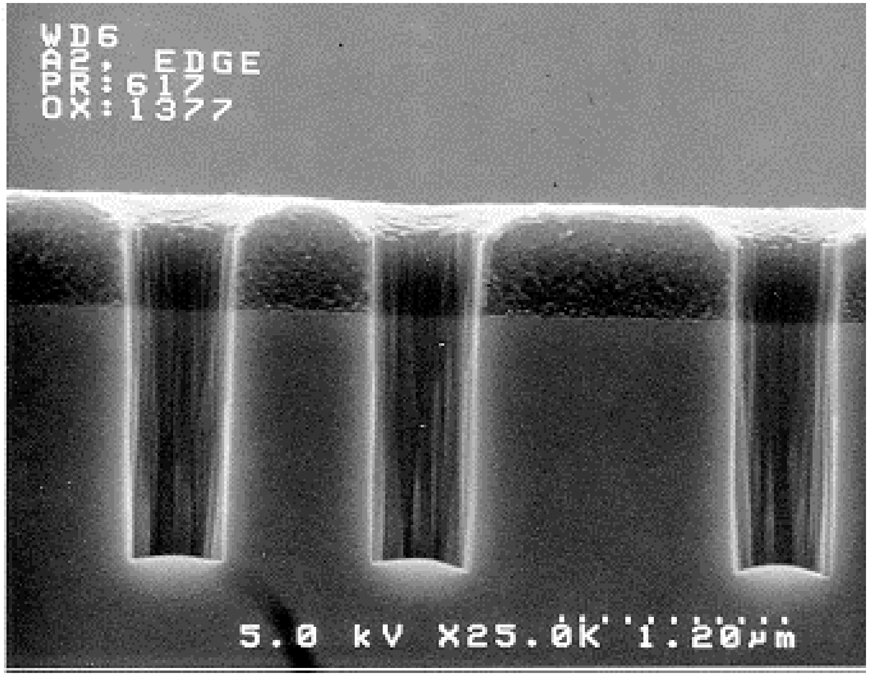
- No surface tension effects
  - Vapors penetrate sub-0.1 micron features (year 2005)
- No contamination from liquid bath
- Cluster tools
  - Wafer protected from atmosphere
  - Tool footprint in fab
  - Single wafer processing



Sources of Metallic Contamination

- Photoresist
- Reactive Ion Etching (RIE) (plasma etching)
- Oxygen Ashing
- Replace HPM (SC-2) with UV/Cl_2

SEM of 0.5 μm Feature After RIE



CD = 0.5 μm
AR = 2.5
HDP Source, post-RIE, before ashing
PR / TEOS

International Technology Roadmap for Semiconductors -- Metal Concentration Goals

Table 21 1999 Short Term Surface Preparation Technology Requirements

Year of Introduction	*2001*	*2002* *130 nm*	*2003*	*2004*	*2005* *100 nm*
Front End of Line (A)					
Critical surface metals (at/cm^2)	🟨 $\leq 6x10^{9}$	🟨 $\leq 4.4x10^{9}$	🟨 $\leq 3.4x10^{9}$	🟥 $\leq 2.9x10^{9}$	🟥 $\leq 2.5x10^{9}$
Metal atoms per Si(100)	1:323,000	— —	— —	— — ▶	1:770,000

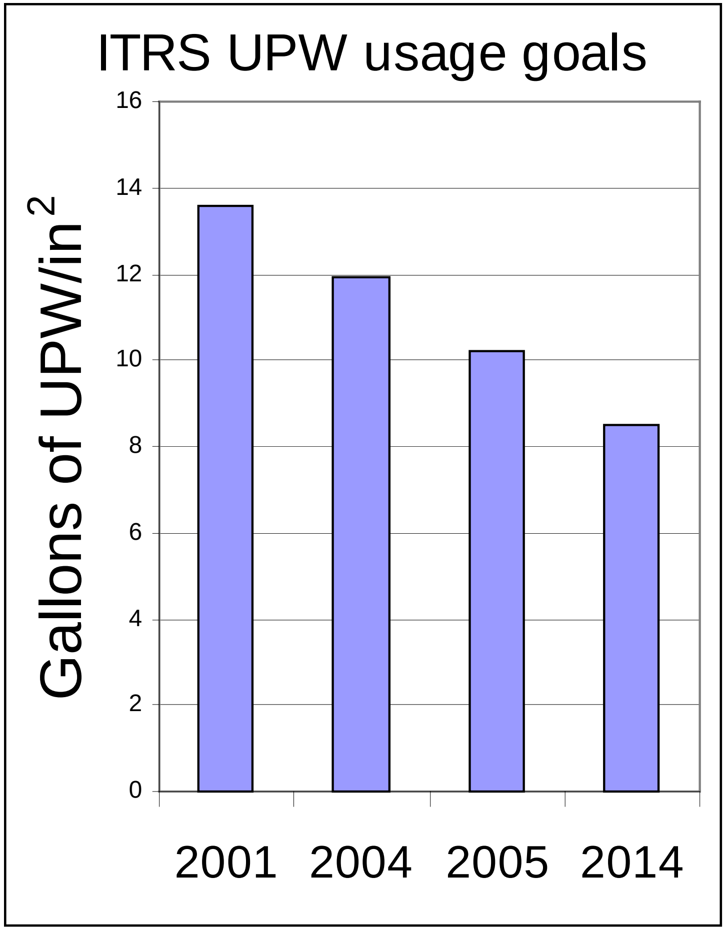
Solutions Exist ⬜ *Solutions Being Pursued* 🟨 *No Known Solution* 🟥

Critical Surface Metals: **Fe[1,4],Ca, Co, Cu[1,3,4], Cr[5], K[1], Mo, Mn, Na[1], and Ni[1,2,4]**

1. Sugino, et al. 2. Courtney and Lamb 3.Chang, et al. 4. Lawing, et al. 5. Ma, et al.

Water Conservation

- Replacing 1/3 of wet cleans with dry cleans saves 216 million gallons of UPW or 324 million gallons of municipal water per year.
    - 1500 8”-wafers/day and 2000 gallons UPW per 8”-wafer
    - Wet cleans consume ~60% of UPW
    - 1.5 gallons of municipal water per 1 gallon UPW
    - (Mendicino, et al, 1999)

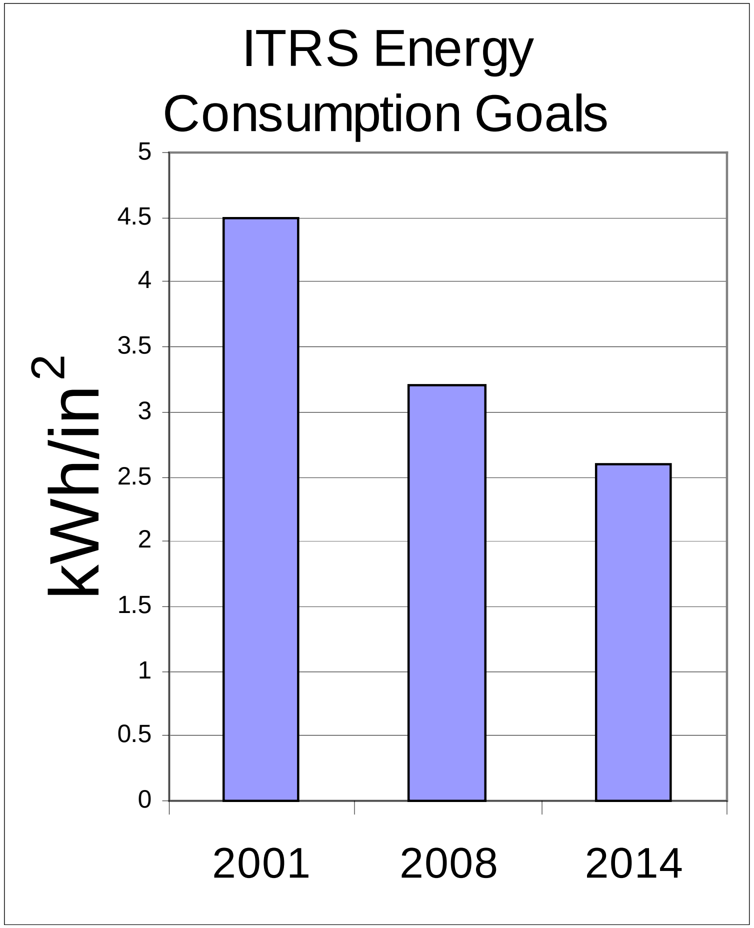


Chemical Usage Reduction

- Chemicals, Materials, and Equipment Management -- Reduced Consumption of Chemicals
  - Elimination of sulfuric acid by 2004
- Dry Cleans can reduce chemical consumption by 1000 times (Chang, et al, 1999).
- Reduced consumption = less waste disposal

Energy Conservation

- At 50 kWh/1000 gallons of UPW (Mendicino, et al, 1999), saving 216 million gallons of UPW conserves 10.8 million kWh of electricity.
- At $0.045/kWh, this saves $486,000/year
- Gains need to be measured against increased usage of vacuum pumps and heaters.



International Technology Roadmap for Semiconductors -- ESH Targets

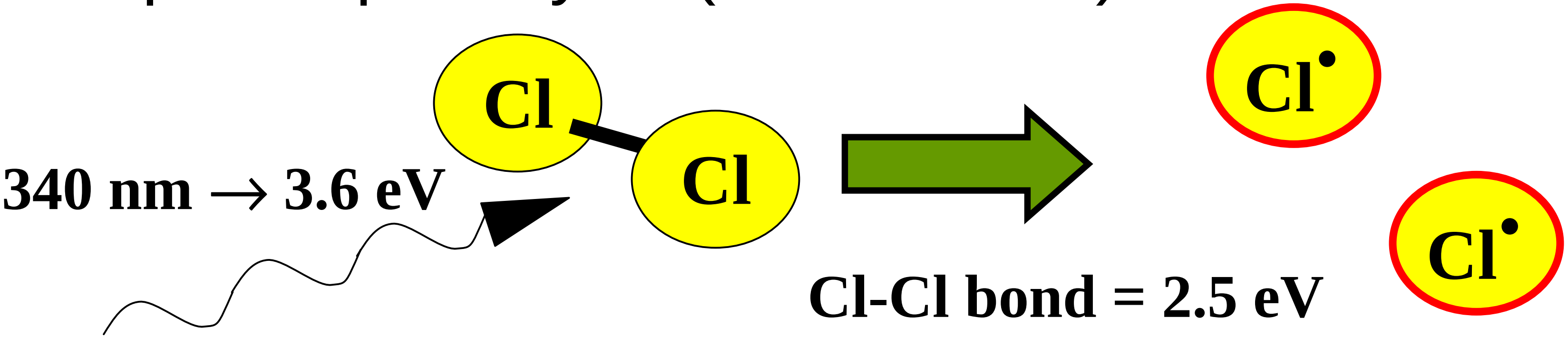
- Workplace Protection -- Reduced Worker Exposure to Hazardous Fumes
  - “Isolate workers from chemicals and byproducts during operation” in 2001
  - “Reduced chemical usage in clean processes” by 2005
  - “Novel rinse/clean methods that reduce water and chemical usage” by 2011

- All fumes/vapors contained within vacuum chamber

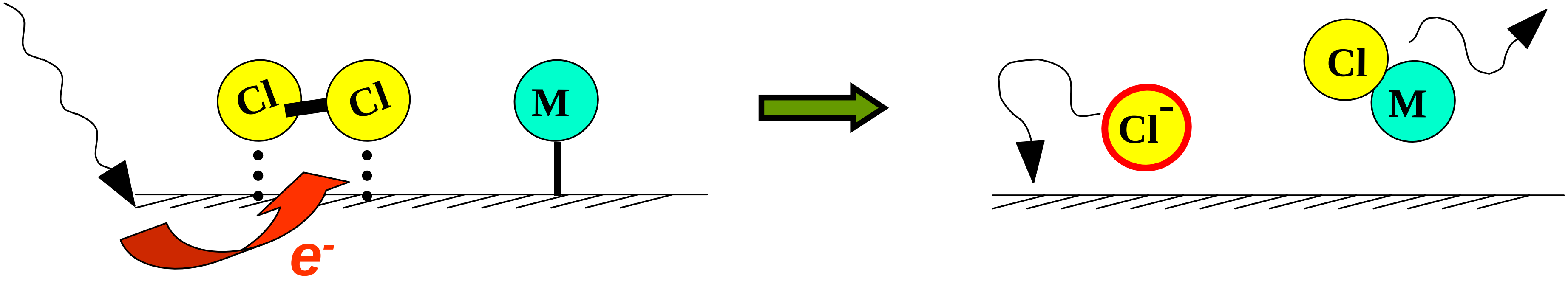
- Thrust B, Wafer Cleaning Resource Consumption for Front End 0.13 μm CMOS Device Process Flow Project

Background Information—UV/Cl_2 Metal Removal

- Gas-phase photolysis (250-400 nm)



- Surface photolysis



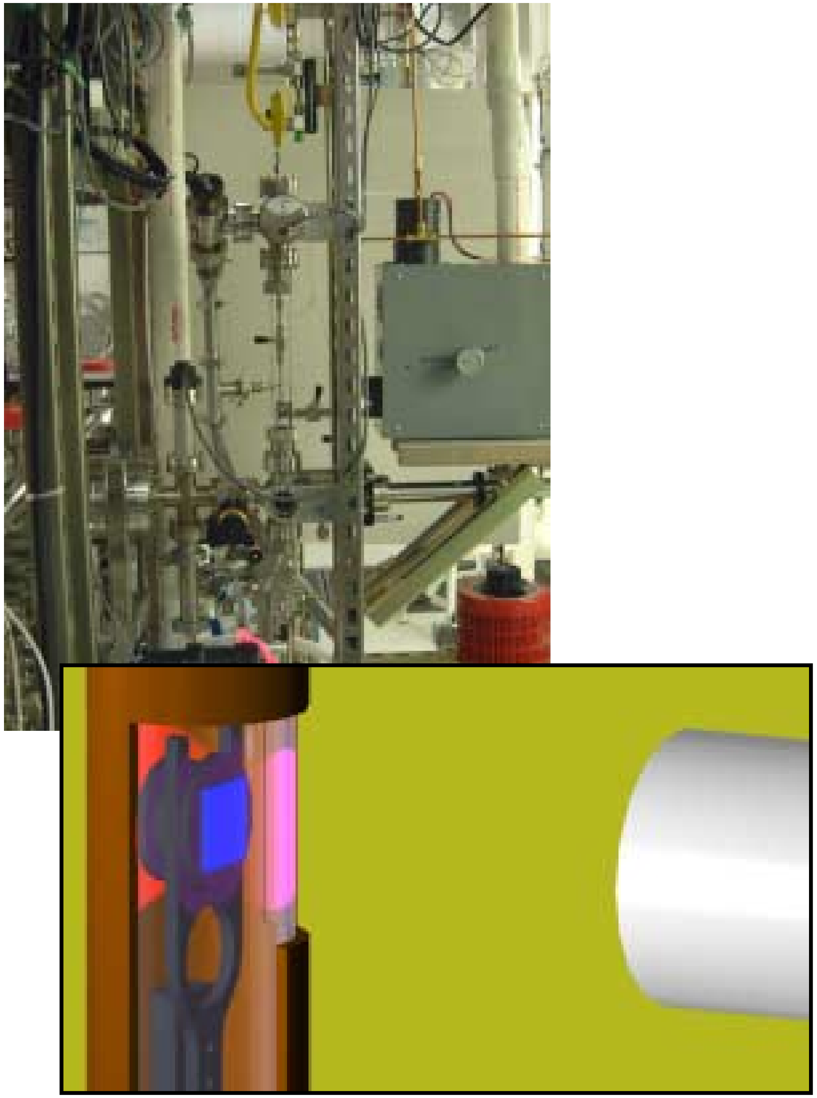
Project Objectives—UV/Cl_2 Metal Removal

- Removal mechanism
  - Volatile products
  - “Lift-Off”
  - Metal-silicon-chlorine complex
- Reaction mechanism and products
  - Gas-phase or surface photolysis
  - Substrate and dopants
  - Oxide thickness
  - Contaminant and its concentration
  - Surface termination and other adsorbed species
- Monochromatic UV source

Thermochemistry

Reaction	ΔG_{rxn} (250°C)	P_{sub} (250°C)
1. $Cu + Cl(g) \rightarrow CuCl$	-219 kJ/mol	4×10^{-5} Torr
2. $Cu + 2Cl(g) \rightarrow CuCl_2$	-322 kJ/mol	4×10^{-7} Torr
3. $CuCl_2 \rightarrow CuCl + \frac{1}{2} Cl_2(g)$	67.4 kJ/mol	
4. $Cu_2O + 2Cl(g) \rightarrow 2CuCl + \frac{1}{2} O_2(g)$	-307 kJ/mol	4×10^{-5} Torr
5. $CuO + Cl(g) \rightarrow CuCl + \frac{1}{2} O_2(g)$	-112 kJ/mol	4×10^{-5} Torr

UV Reactor Schematics



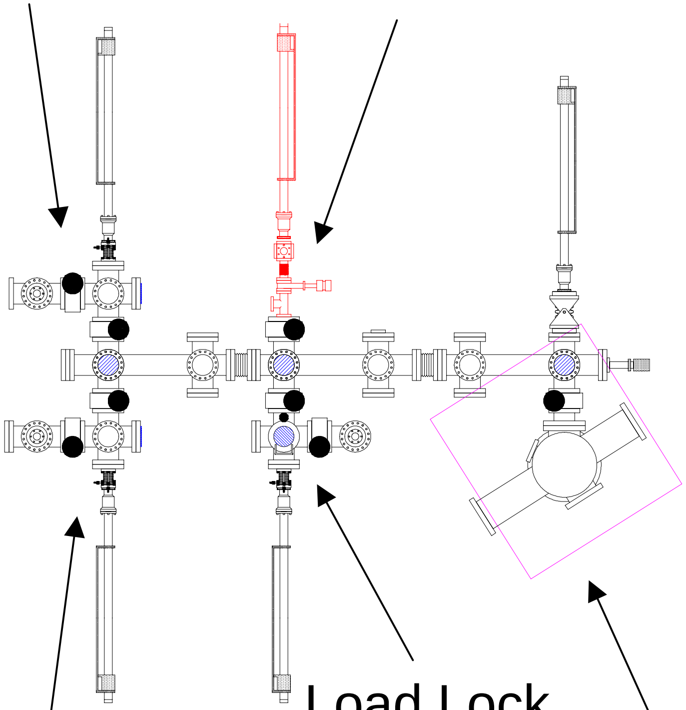
Reactor

- 5 - 50 sccm Cl_2 flowrate
- Pressure (100 - 1000 mTorr)
- Temperature (21 - 300^{o}C)
- 1000-Watt Xe arc lamp (~250 mW/cm^2 at sample)

Future Plans

- Install Monochromator
- Residual Gas Analyzer (RGA) to identify reaction products
- UV/O_3 for carbon removal

Integrated Processing Apparatus



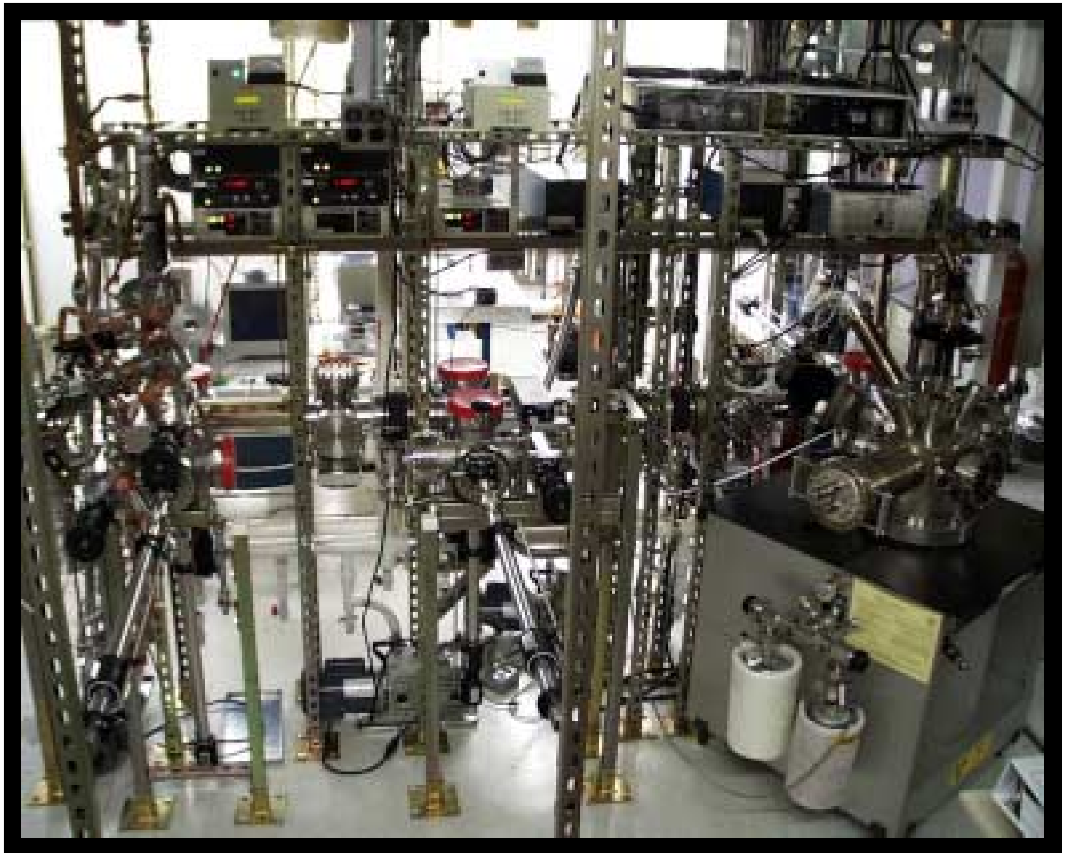
UHV SSC reactor

Photochemistry reactor

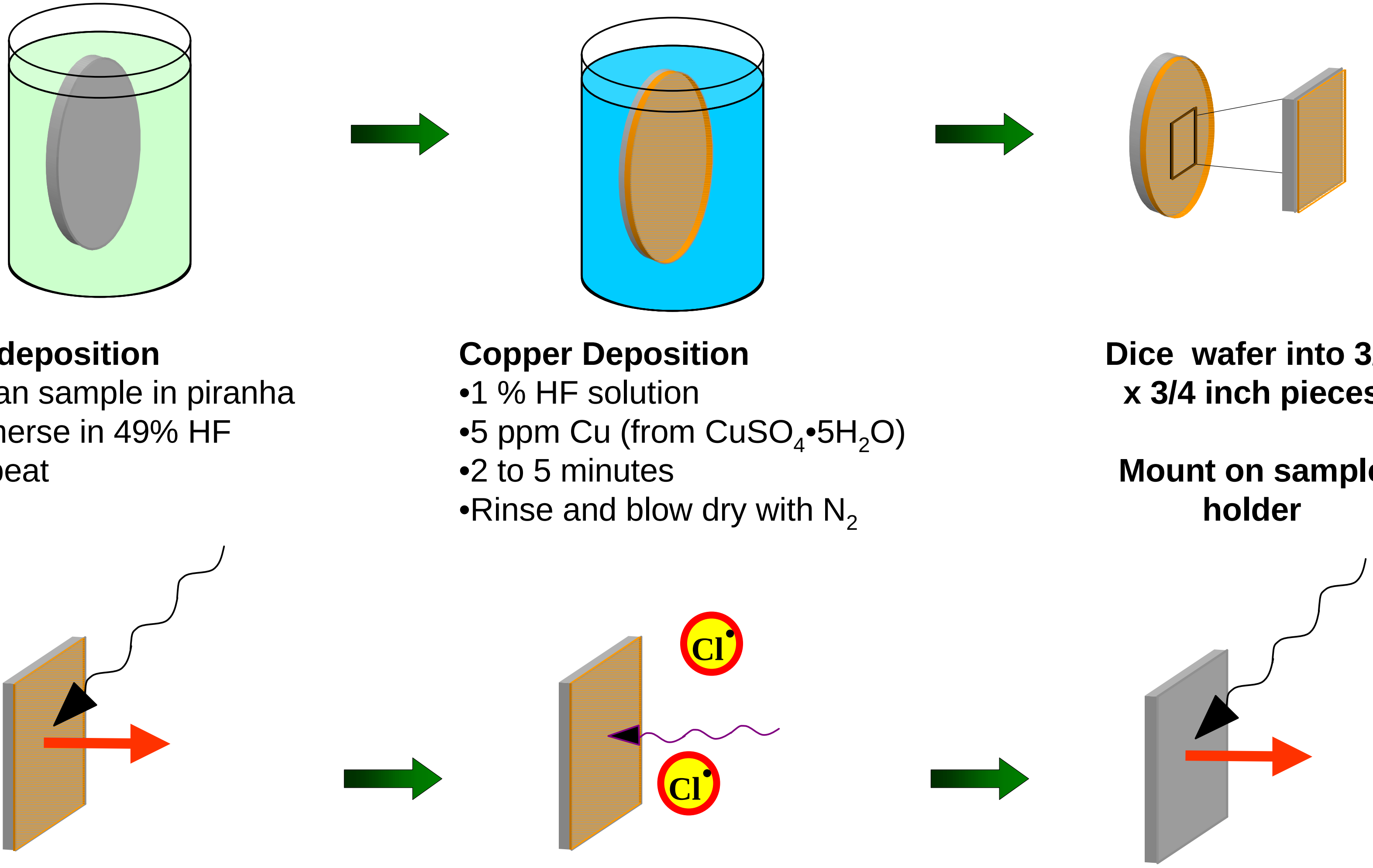
Load Lock

HF/Vapor Phase Etching Reactor

Ultra High Vacuum Surface Analysis Chamber



Experimental Procedure



Pre-deposition
- Clean sample in piranha
- Immerse in 49% HF
- Repeat

Copper Deposition
- 1 % HF solution
- 5 ppm Cu (from $CuSO_4•5H_2O$)
- 2 to 5 minutes
- Rinse and blow dry with N_2

Dice wafer into 3/4 x 3/4 inch pieces

Mount on sample holder

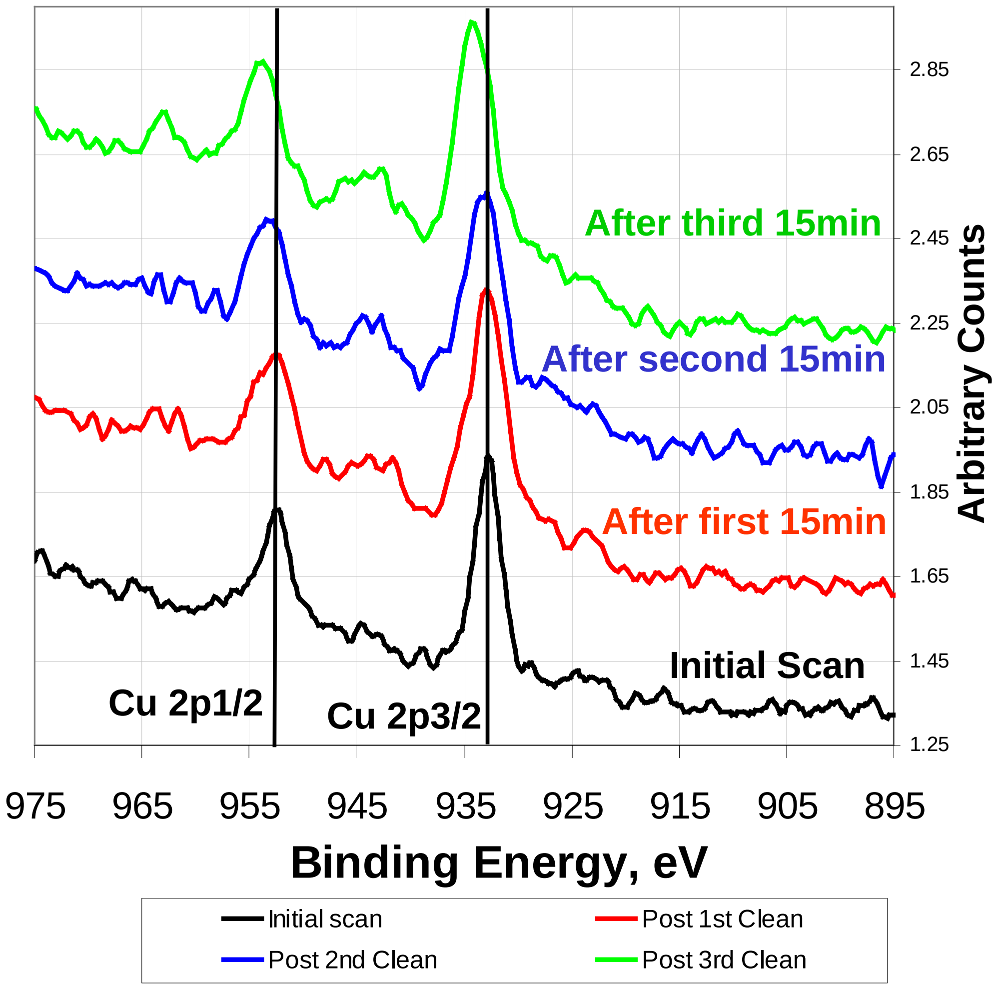
Pre-copper removal XPS scan

Copper Removal with UV/Cl_2

Post-copper removal XPS scan

Preliminary Results, UV/Cl_2 Copper Removal

XPS spectra showing copper removal at room temperature



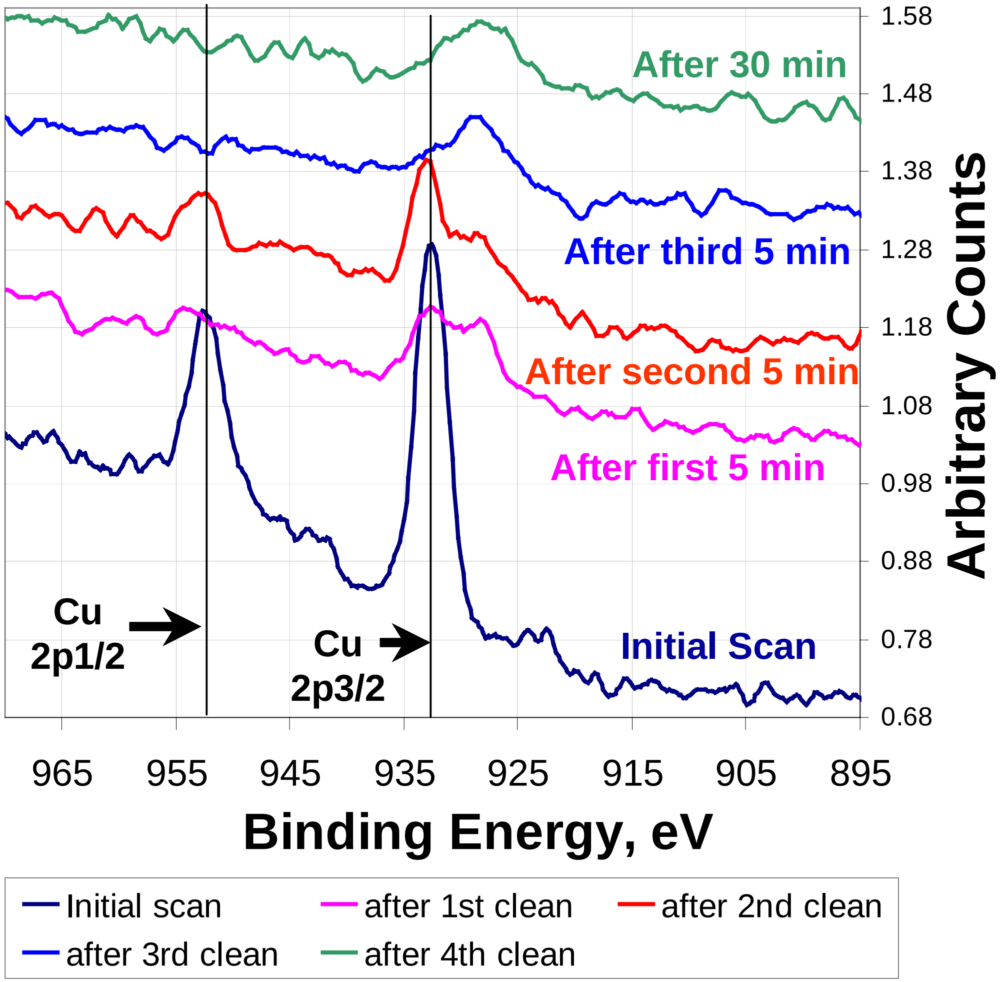
- Experimental Conditions
  - Nominally 21°C
  - Reactor pressure 300 mTorr, 30 mTorr Cl2
- Results
  - $CuCl_2$ at room temperature

    $Cu + 2Cl(g) \rightarrow CuCl_2$

  - No significant removal of copper

Preliminary Results, UV/Cl_2 Copper Removal

XPS spectra showing removal of copper at 200° C



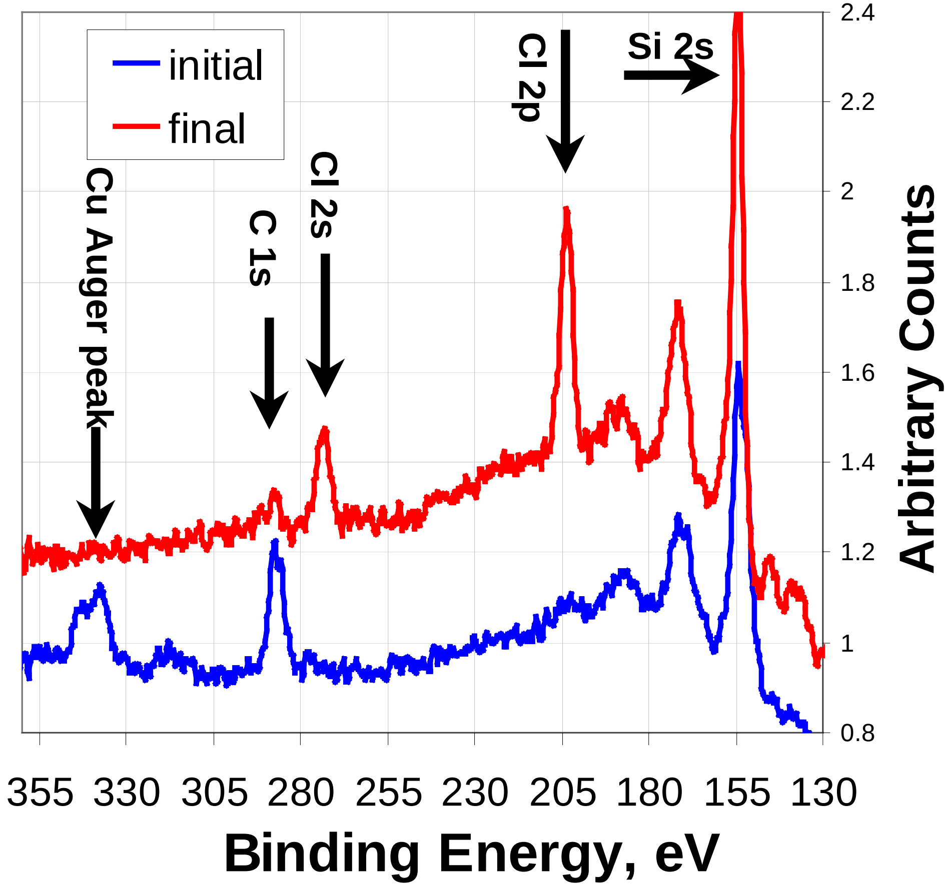
- Experimental Conditions
  - Reactor pressure 300 mTorr, 30 mTorr Cl_2
- Results
  - High temperature induced formation of CuCl
  - Chemical shift stronger than expected
  - Copper concentration decreased
  - Unable to achieve total removal, even after two additional 1-hour cleans

Future Plans

- Calibrate reactor temperature
- Calibrate XPS for copper concentration
- Complete Removal of Copper
  - Higher Cl_2 concentration
  - Low temperatures (100°C or lower)
- Oxide wafers
- Integrated Processing
- Look for wavelength dependence
  - Removal and reaction mechanisms
  - Removal efficiency
  - Oxidation state of metal chloride surface species
- Verify conclusions with TXRF
- Other metals

Preliminary Results, Carbon Removal

XPS spectra showing decrease in carbon signal during copper removal experiment.



- Experimental Conditions
  - nominally 150°C
  - Reactor pressure 500 mTorr, 147 mTorr Cl_2
  - 90 minute reaction time.
- Results
  - Carbon signal decreased.
  - Inconsistant carbon removal

Summary

- ITRS goals
  - Reduced consumption of Water, Energy, and Chemicals
  - Reduced worker exposure
- Processing benefits
  - Cluster Tools
  - Clean small features
- UV/Cl_2 Metal Removal
  - Nickel, copper, iron, sodium, potassium, calcium, chromium, and zinc
  - Reaction and removal mechanisms
  - Monochromatic light source
- Carbon Removal

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