Removal of Metals from Semiconductor Surfaces Using Dry Cleaning Methods

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SRC Benign Manufacturing

Motivation

- Gate dielectric thicknesses are approaching native oxide thickness—cluster tool!!!!
- Cluster tool
  - One wafer, dry clean
  - Rapid thermal oxidation (RTO) and annealing (RTA)
  - Poly Si deposition

Wet Cleans

SC-1 (standard clean 1)

- H_2O_2—hydrocarbon removal
- NH_4OH--particle removal, oxide etch

SC-2 (standard clean 2)

- H_2O_2—oxidize surface (metals and hydrocarbons)
- HCl—make soluble metals

HF—hydrogen flouride

- HF—oxide etch

Wet clean mechanisms

- Hydrocarbons

  $C_xH_y + H_2O_2 \rightarrow CO_2 + H_2O$
- Oxide

  $SiO_2 + NH_4OH \rightarrow Si(OH)_4 + NH_3$

  $SiO_2 + HF \rightarrow SiF_4 + H_2O$
- Metals

  $MO_x + HCl \rightarrow MCl_n + H_2O$
- Particles
  - Zeta potential

Dry Clean Mechanisms

- Hydrocarbons

  $C_xH_y + O_3 + h\nu \rightarrow CO_2 + H_2O$

- Oxide

  $SiO_2 + HF \rightarrow SiF_4 + H_2O$

- Metals

  $MO_x + Cl_2 + h\nu \rightarrow MCl_n + O_2$

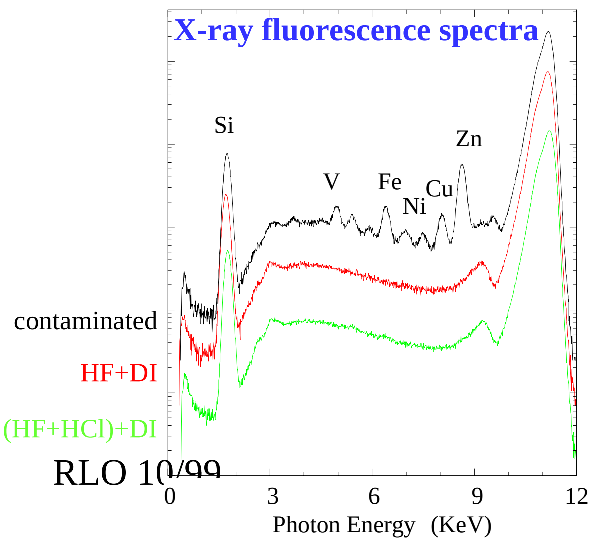
- Particles?????

Metal Chloride Boiling Points

KCl	subl 1500 C
$CaCl_2$	> 1600 C
$TiCl_4$	136 C
VCl_4	148 C
$MnCl_2$	1190 C
$FeCl_2$	d 315 C
$CoCl_2$	1049 C
$NiCl_2$	973 C
CuCl	1490 C
$CuCl_2$	993 C
$ZnCl_2$	732 C

Wafer Cleaning in IC Manufacturing

	Wet Clean	Dry Clean
Metals	H_2SO_4/H_2O_2/DI, HCl/H_2O_2/DI, DHF	Cl_2, HCl (UV, plasma)
Particles	NH_4OH/H_2O_2/DI	cryogenic aerosol, CO_2 snow
Organics	H_2SO_4/H_2O_2/DI, NH_4OH/H_2O_2/DI	O_3, O_2 (UV or plasma)
Native oxide	dHF, bHF	AHF/H_2O(alcohol), H_2(UV, plasma)
UPW usage	high	low
Chemical usage	high	low
Foot-print	large	small
Worker's risk	high	low



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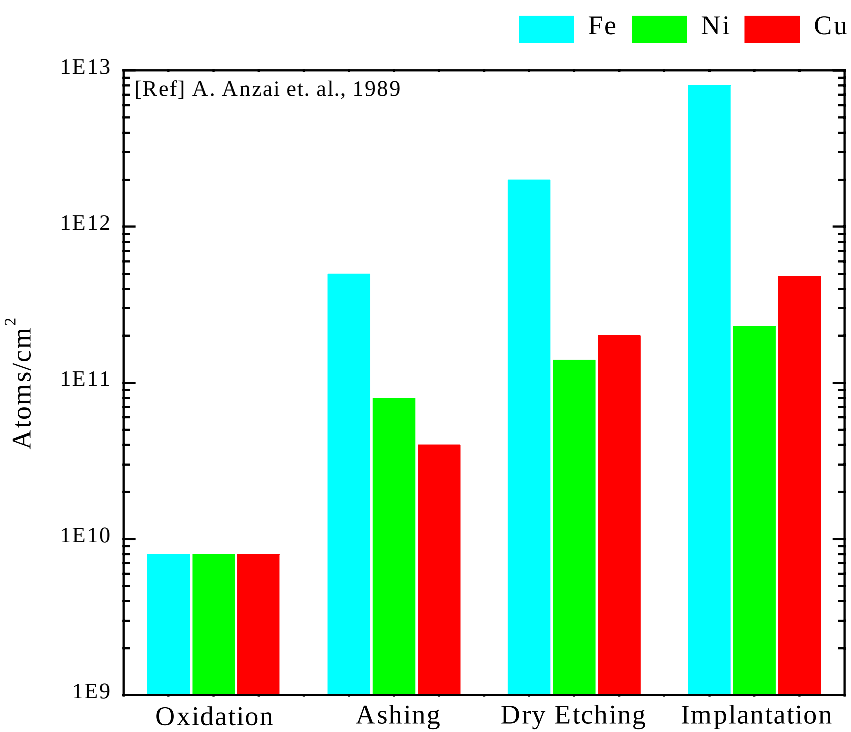
Key Issues in Dry Cleans

- Develop gas phase alternatives
- Characterize gas phase reactions
- Characterize surface kinetics
  - — Surface cleanliness (TXRF, XPS)
  - — Surface passivation (in situ XPS, FTIR)
  - — Surface roughness (AFM, STM)
- Characterize electrical performance

Origins of Metal Contamination



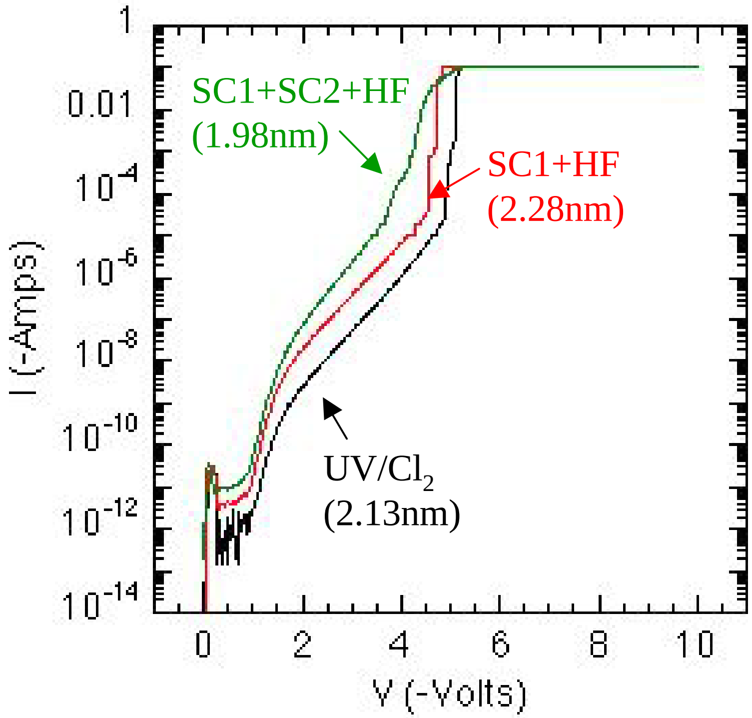
Element	Electron Negativity
Au	2.4
Pt	2.2
Ag	1.9
Hg	1.9
Cu	1.9
Si	1.8
Pb	18
Sn	1.8
Ni	1.8
Fe	1.8
Zn	1.6
Al	1.5
Mg	1.2
Ca	1.0
Na	0.9
K	0.8

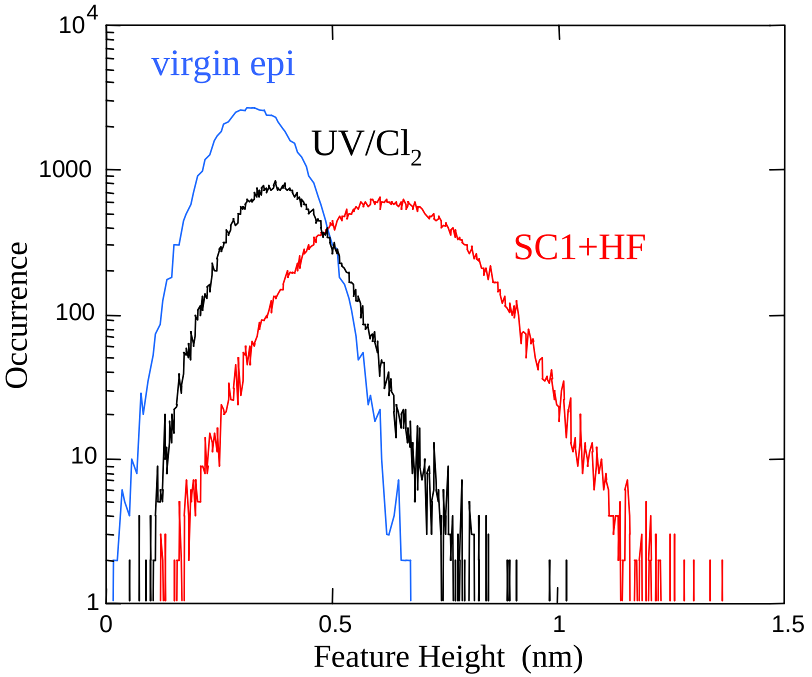
Easier to precipitate on bare silicon surface

- Sources: equipment, processes, materials, and human
- Transition metals precipitation on silicon surfaces is critical

Can Dry Clean Compete with Wet Clean?

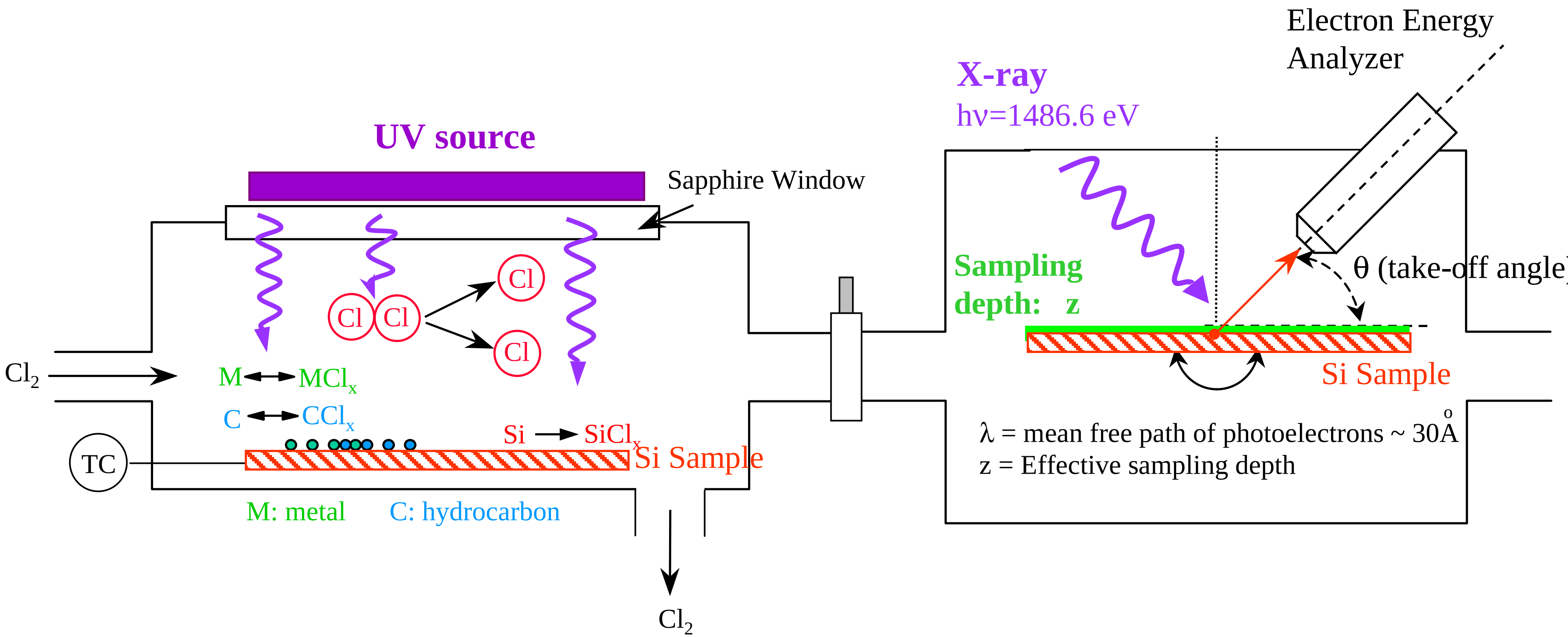
Timp, Sorsch, Sapjeta, Weir, Bell Labs, Lucent Technologies, MRS (1997)





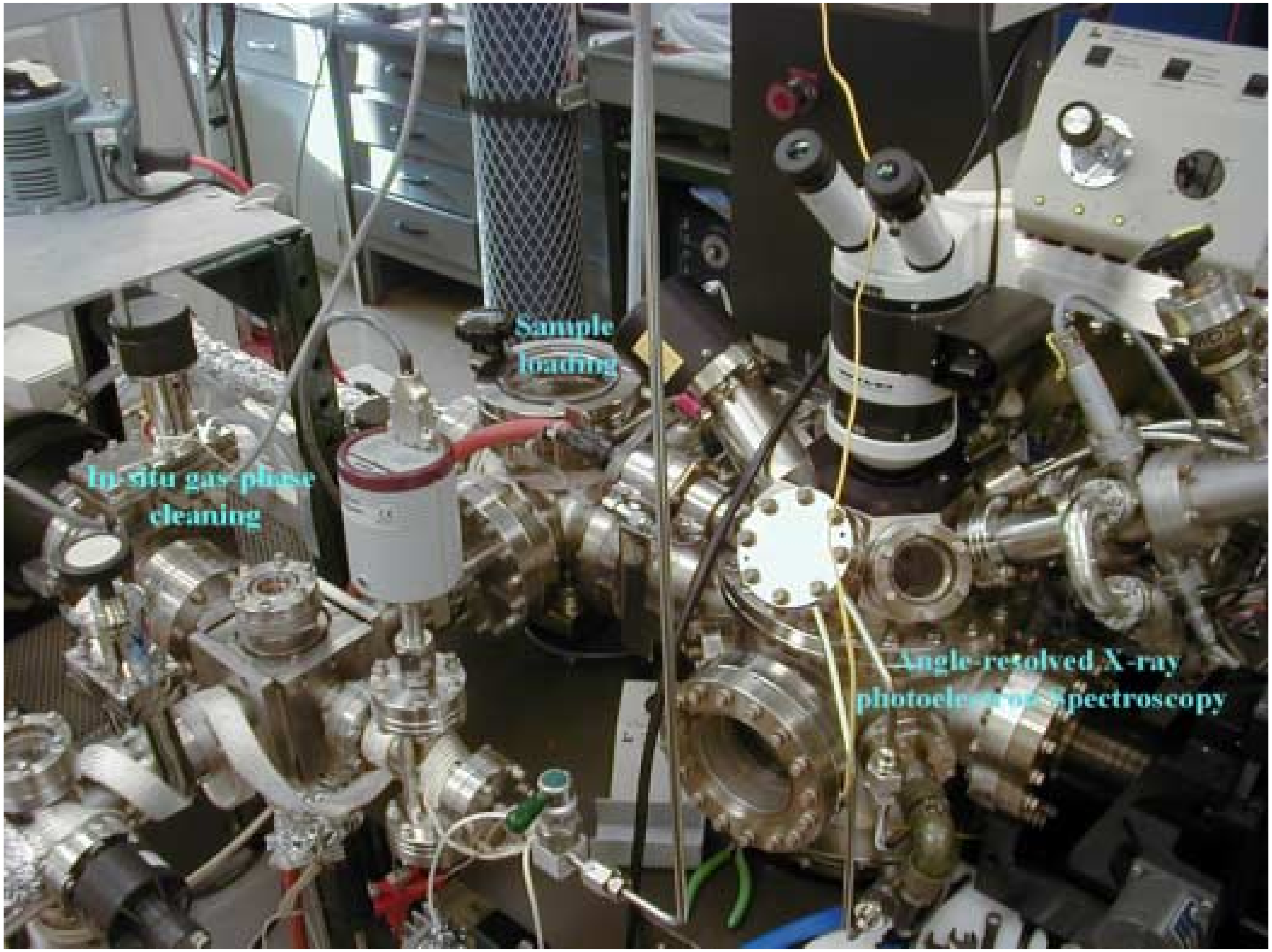
- Concerns:
  - — Metal contamination
  - — Hydrocarbon contamination
  - — Surface termination/chemical states
  - — Surface roughness
- Impact on subsequent processes

UV Cleaning Process



- UV radiation initiates gas-phase reaction and surface reaction
- Remove metallic/organic contamination with UV/Cl_2
- In situ XPS analysis and ex situ TXRF analysis

In-situ XPS and UV Process System



- *In situ* quantification of transition metal concentrations with cleaning processes

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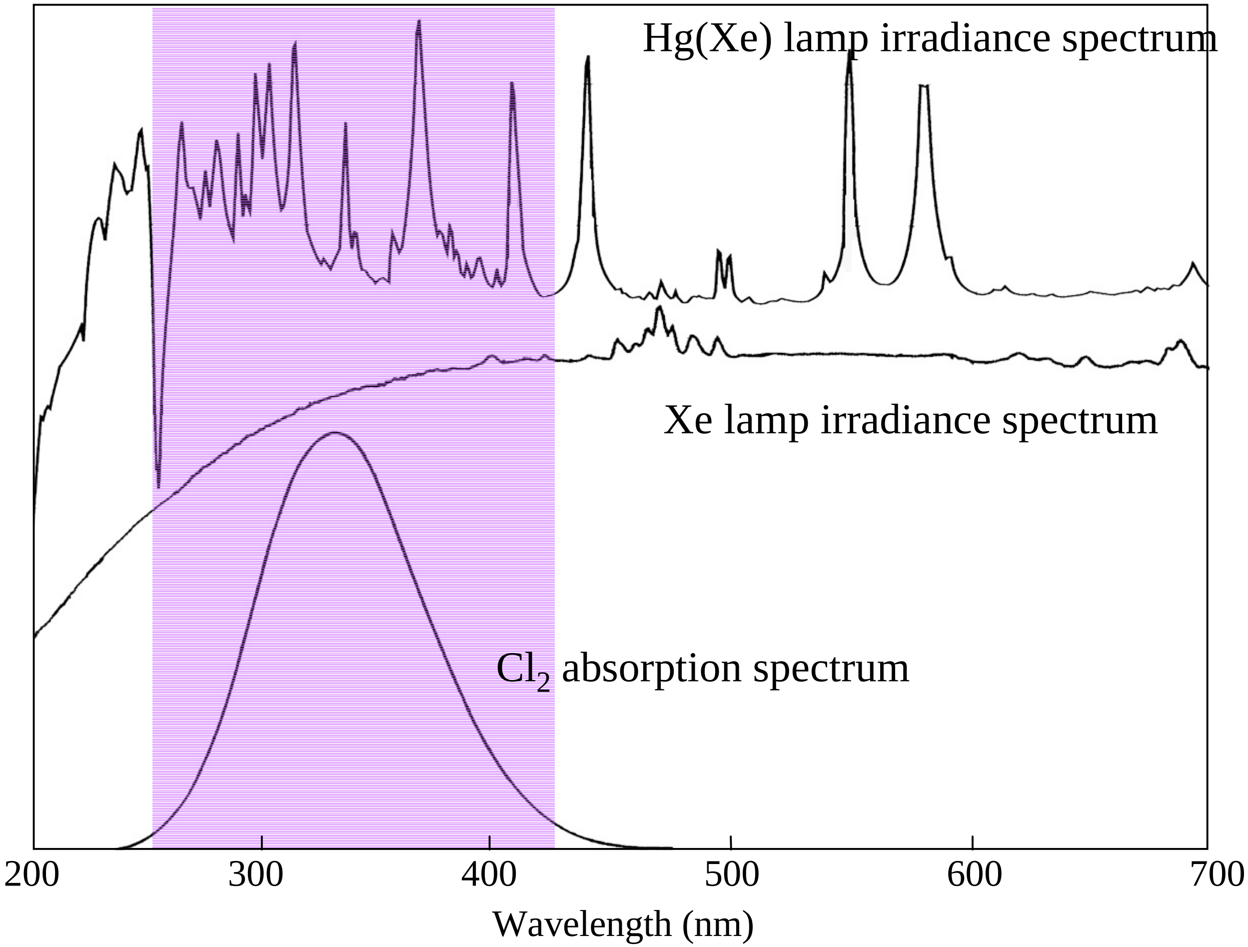
UV/Chlorine Processing

$$Cl_2(^1\Sigma_g^+) + h\nu \rightarrow Cl_2\ (^3\Pi_{o^+u}) \rightarrow Cl(^2P_{3/2}) + Cl(^2P_{1/2})$$

$$\searrow \quad Cl_2\ (^3\Pi_{1u}) \rightarrow 2\ Cl(^2P_{3/2})$$



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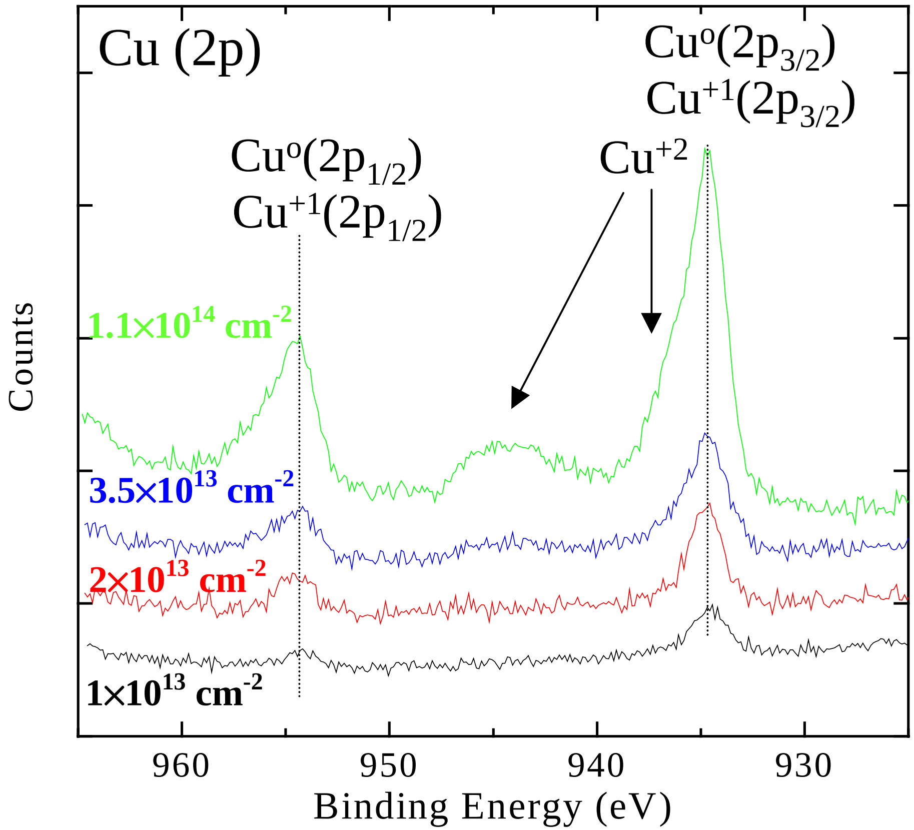
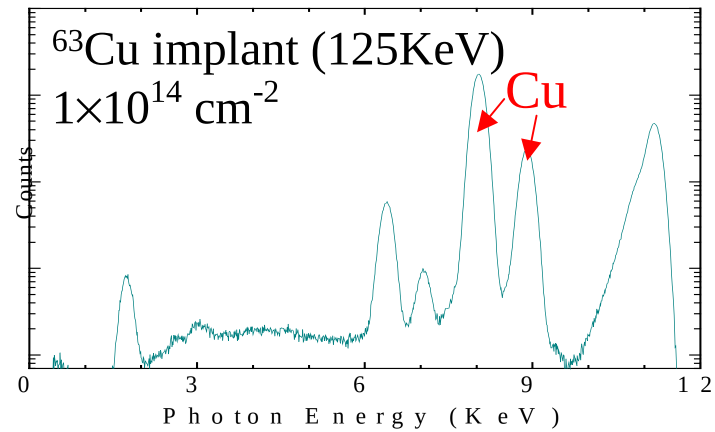
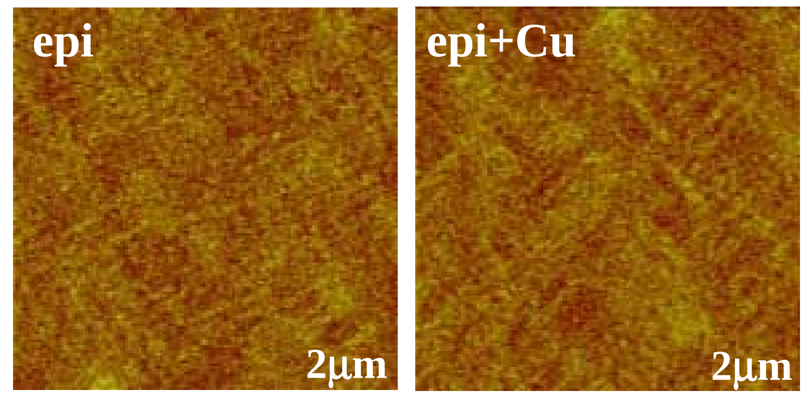
- Broad band radiation vs. monochromatic radiation

Sample Preparation

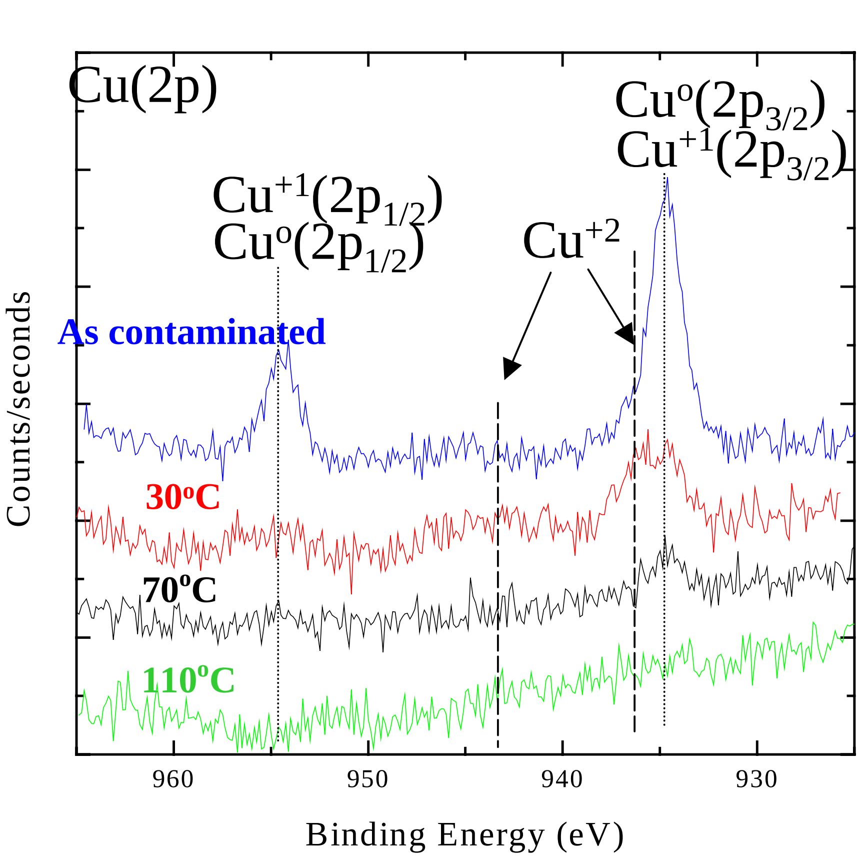


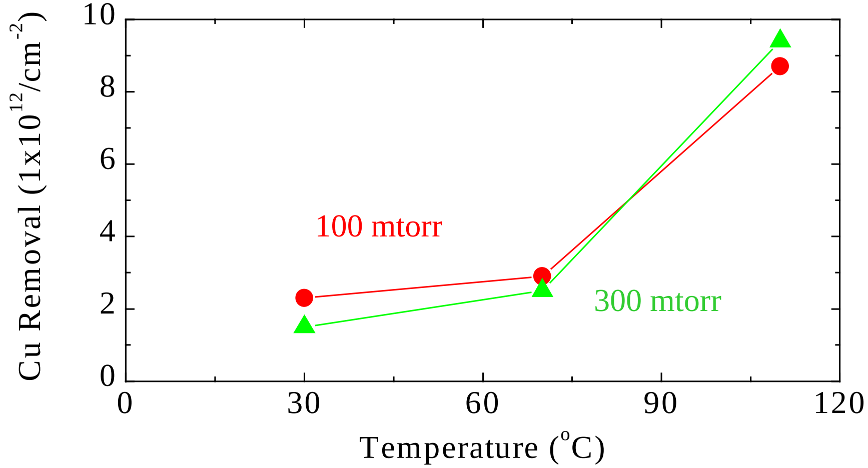


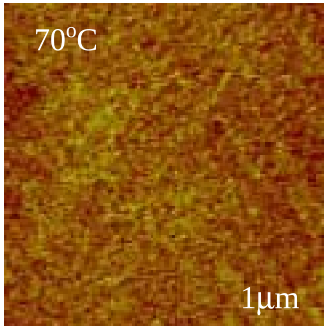


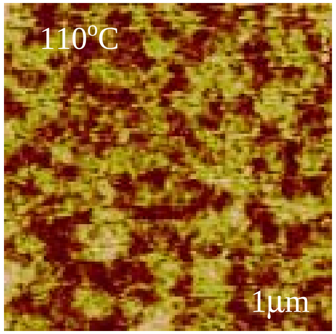
- Contamination of Choice: Cu
  - — Silicon samples contaminated in 1000µg/ml copper atomic absorption standard solution (matrix: 5% HNO_3)
- Surface contamination (10^{13}-10^{14}/cm^2) calibrated with Synchrotron-TXRF analyzed standards
- No surface roughening observed after metal contamination (~1Å)

Copper Removal at High Temperatures









- Cl_2 pressure: 100 mtorr, UV exposure time: 10 min
- $CuCl_2$ formed after UV/Cl_2 exposure
- Complete copper removal at above 100^{o}C

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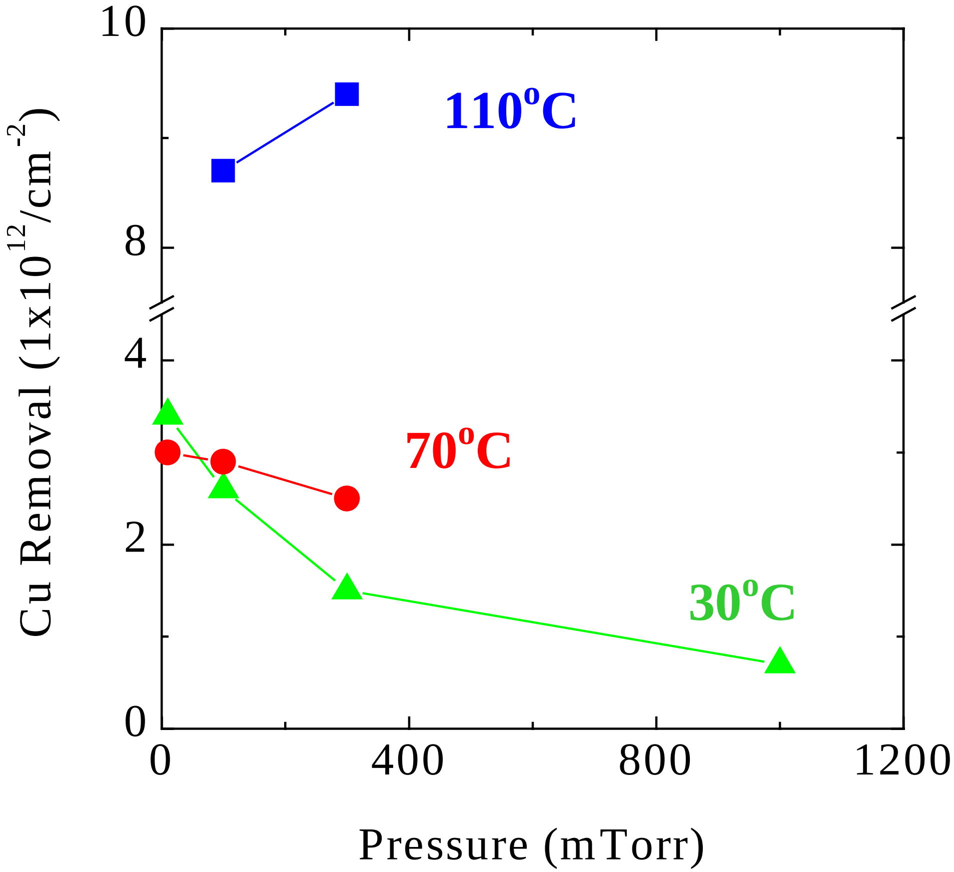
Effect of Chlorine Pressure



- Copper removal efficiency is inversely proportional to the Cl_2 pressure at room temperature
- Copper removal efficiency depends less on the Cl_2 pressure at higher temperatures

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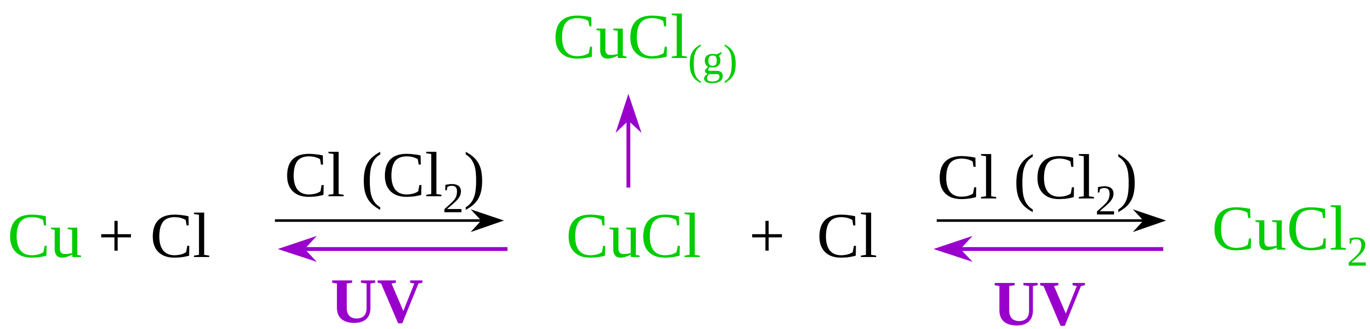
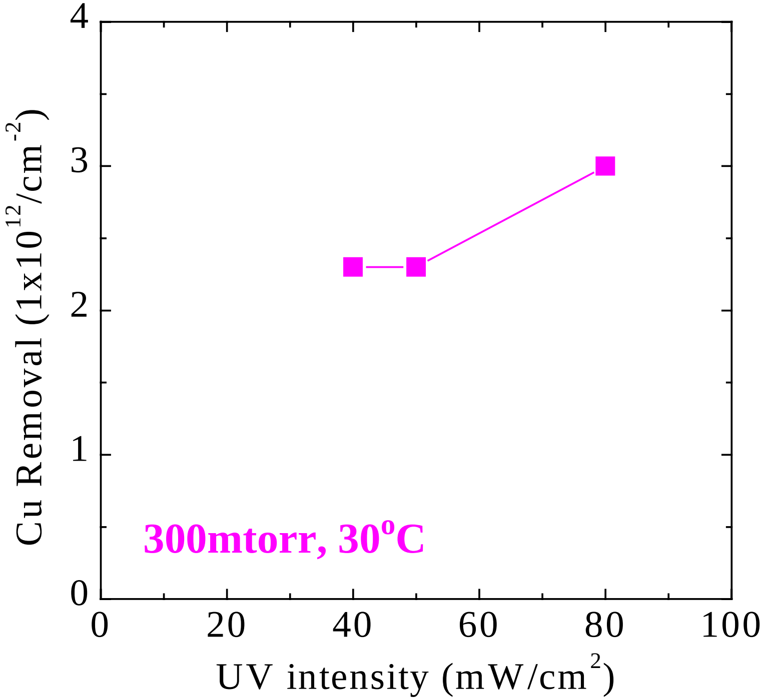
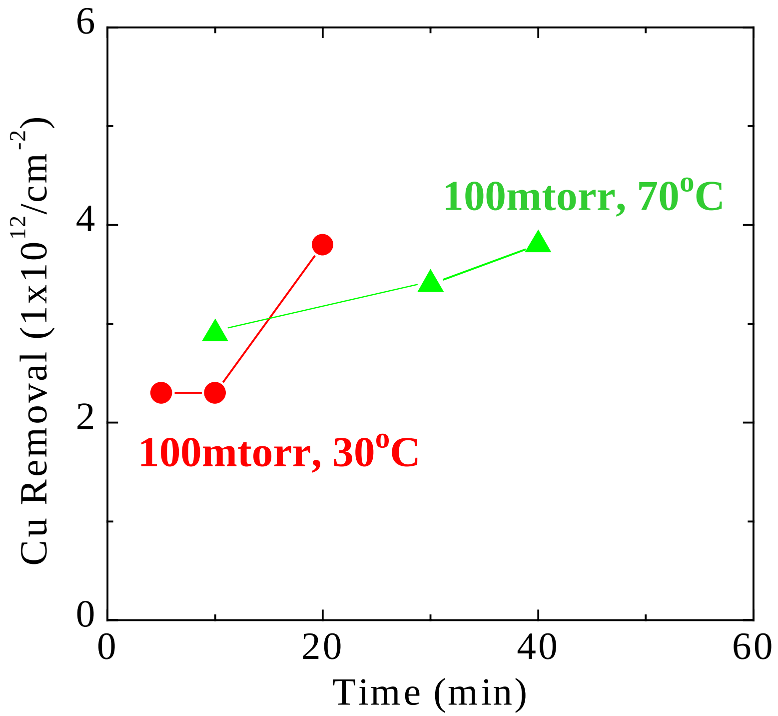
Copper Removal Mechanism



- UV enables the production of atomic chlorine (350-375nm) and enhances the formation of non-volatile $CuCl_2$
- UV enables chemical reduction of metal chlorides (235-245nm) and allows metal removal at relatively low temperatures
- Thesis (Lawing, MIT), Patent (Lawing, Chang, Sawin and FSI)

Effect of UV Exposure



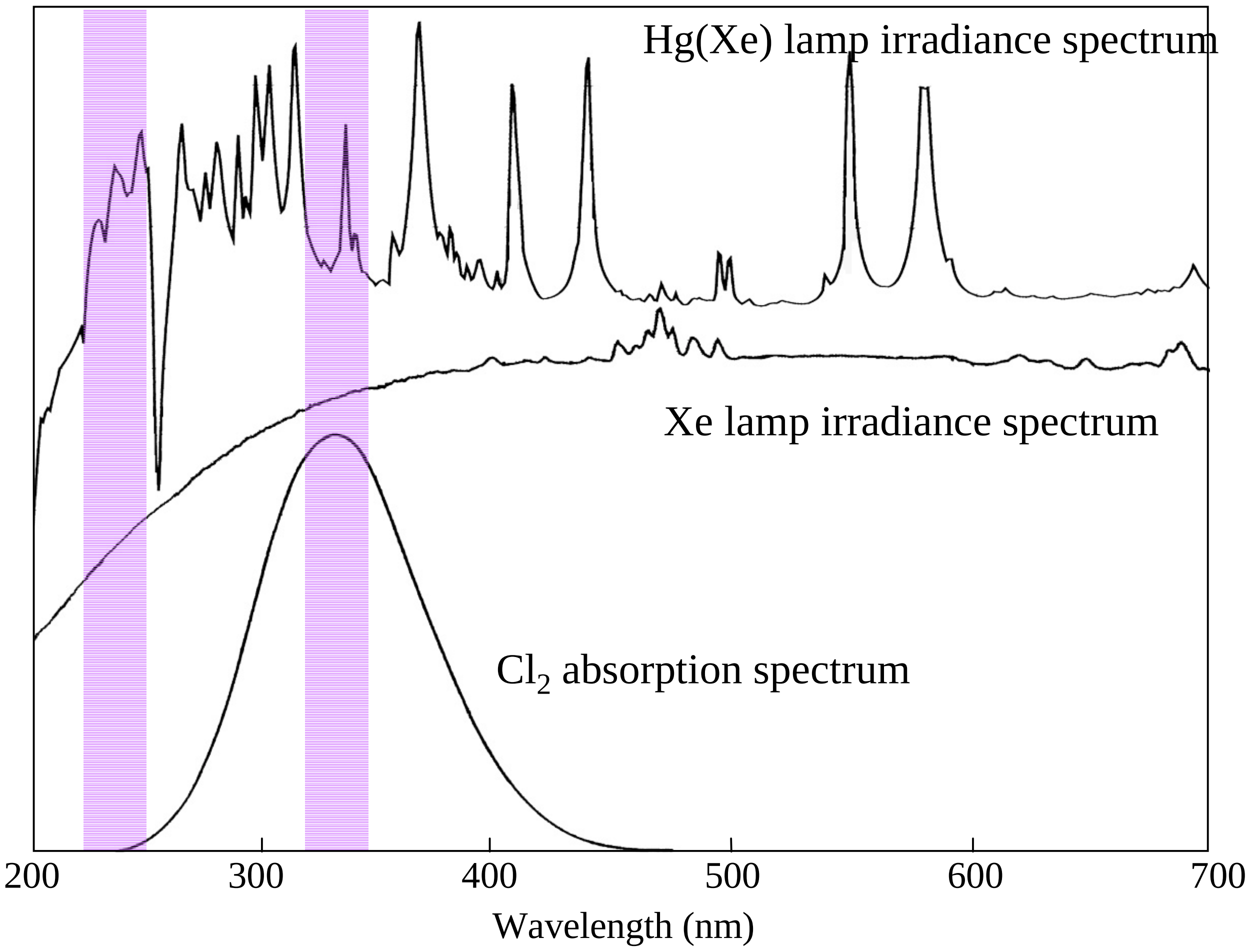


- Copper removal efficiency increases with UV intensity and exposure time

Monochromatic UV Radiation

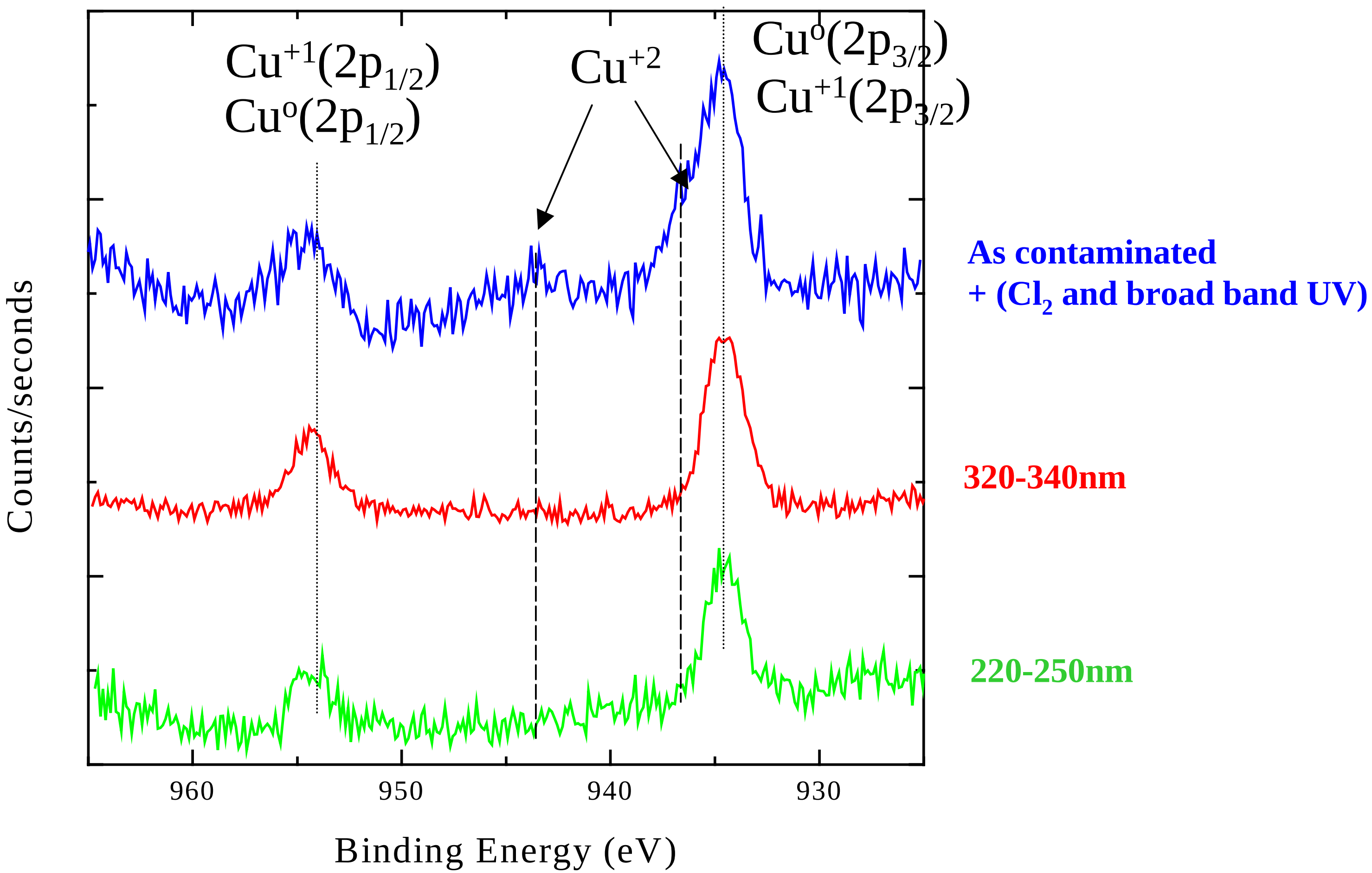
$$Cl_2(^1\Sigma_g^+) + h\nu \rightarrow Cl_2\ (^3\Pi_{o^+u}) \rightarrow Cl(^2P_{3/2}) + Cl(^2P_{1/2})$$

$$\searrow \quad Cl_2\ (^3\Pi_{1u}) \rightarrow 2\ Cl(^2P_{3/2})$$



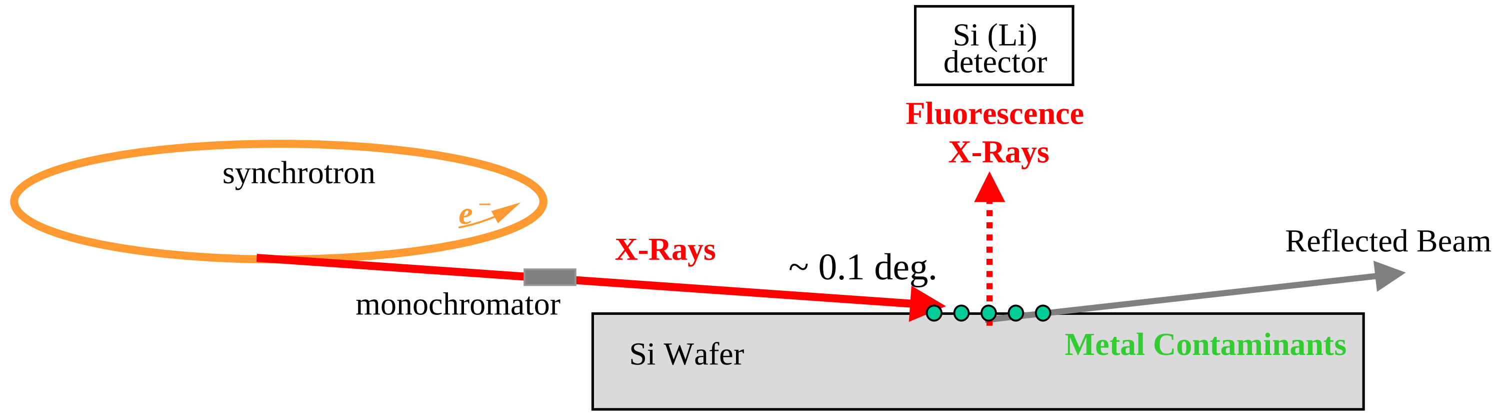
- Monochromatic radiation (low UV intensity) at 330nm and 240nm

Effect of UV Wavelengths

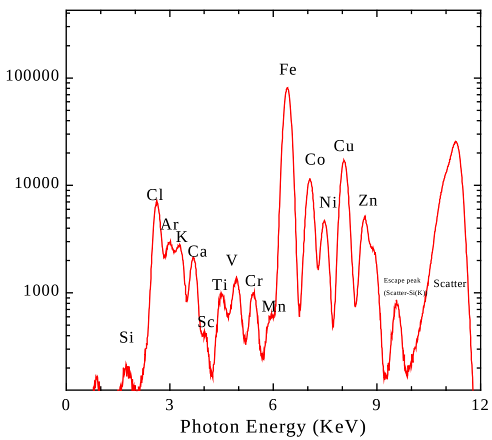


- $CuCl_2$ formed after UV/Cl_2 exposure
- Monochromatic UV achieved limited Cu removal
- Much longer process time (~ 3 hours) due to low UV intensity

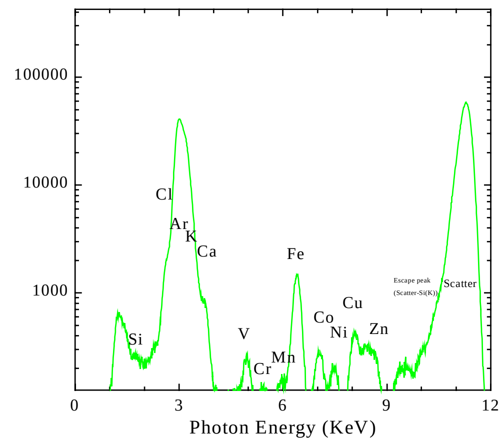
Synchrotron Total Reflection X-ray Fluorescence

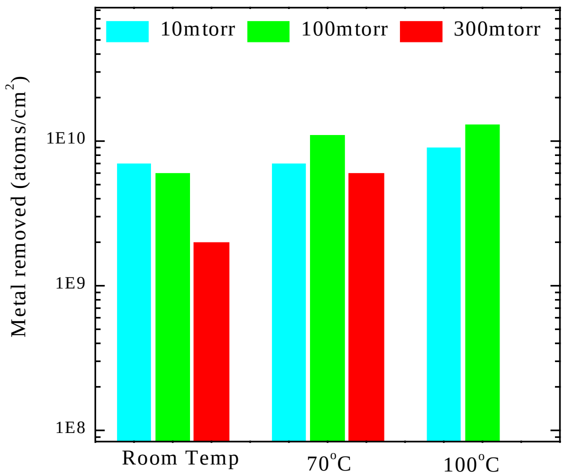


as contaminated



UV/Cl_2 cleaned





- Detection limit for transition metals ~ 3×10^8 atoms/cm^2
- Cu removal efficiency increases with temperature
- Cu removal efficiency depends less on pressure at higher temperature

Conclusion

- UV enhanced the formation of volatile copper chlorides and their subsequent removal
- Metal removal efficiency depends strongly on substrate temperature, moderately on pressure and UV exposure
- Surface roughening is observed after high temperature UV/Cl_2 processing
- SR-TXRF offers leading edge analytical capability with greatly improved detection limits
- Utilized temperature programmed desorption technique to determine the identity of UV/Cl_2 induced volatile surface species
- Investigate removal efficiency of other metals (Fe, Ni, Ca, …)

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