UV-Initiated Surface Preparation and Reaction on Semiconductor Wafer Surfaces

Casey Finstad

cfinstad@engr.arizona.edu

Department of Chemical and Environmental Engineering

University of Arizona

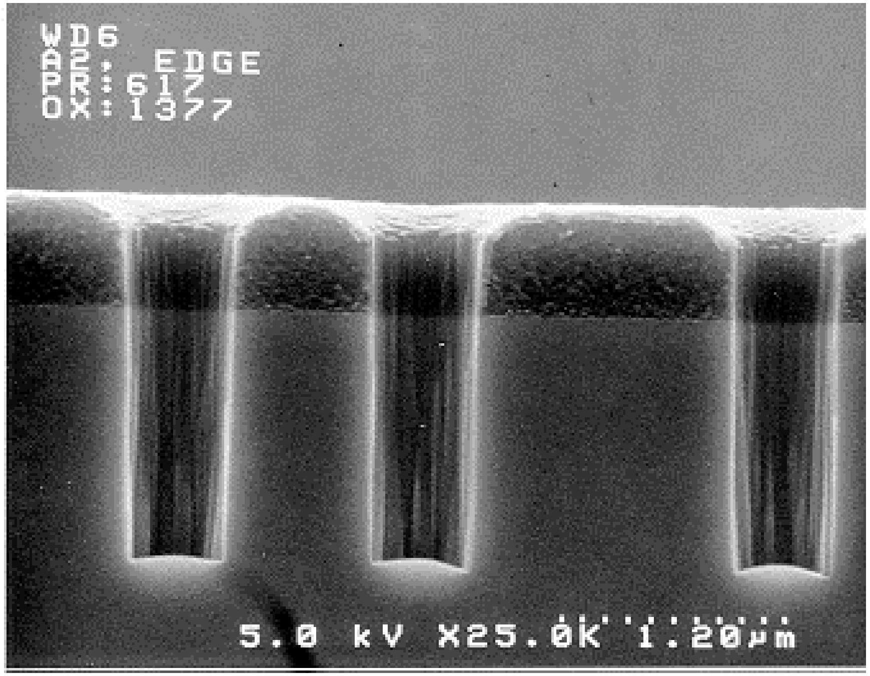
Outline

- UV-initiated surface preparation
  - UV/Cl_2 metals removal
- Experimental Setup
- UV-initiated surface reactions
  - UV-enhanced Atomic Layer Deposition (ALD)
- Summary

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

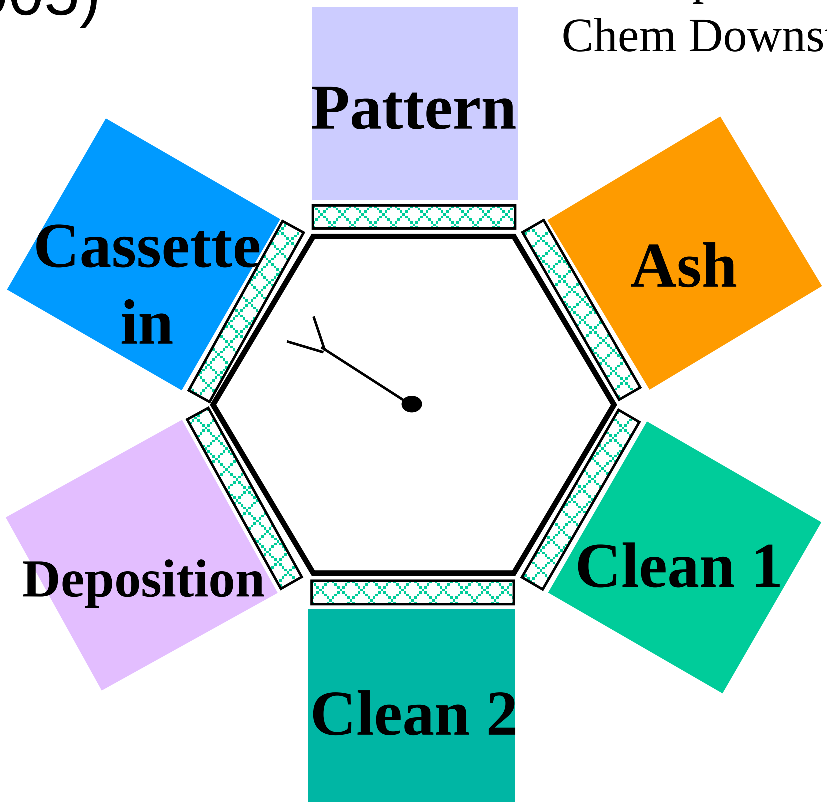
Front End Cleaning Steps

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)	• UV-O_3 • UV-Cl_2

Motivation — UV/Cl_2 Metal Removal

- No surface tension effects
  - Vapors penetrate sub-0.1 micron features (year 2005)
- No contamination from liquid bath
- Cluster tools
  - Wafer protected from atmosphere
  - No worker exposure

$UV\text{-}O_3$
$UV\text{-}F_2\text{-}H_2$
$UV\text{-}ClF_3$
HF/Vapor
Chem Downstream



ESH Significance —UV/Cl_2 Metal Removal

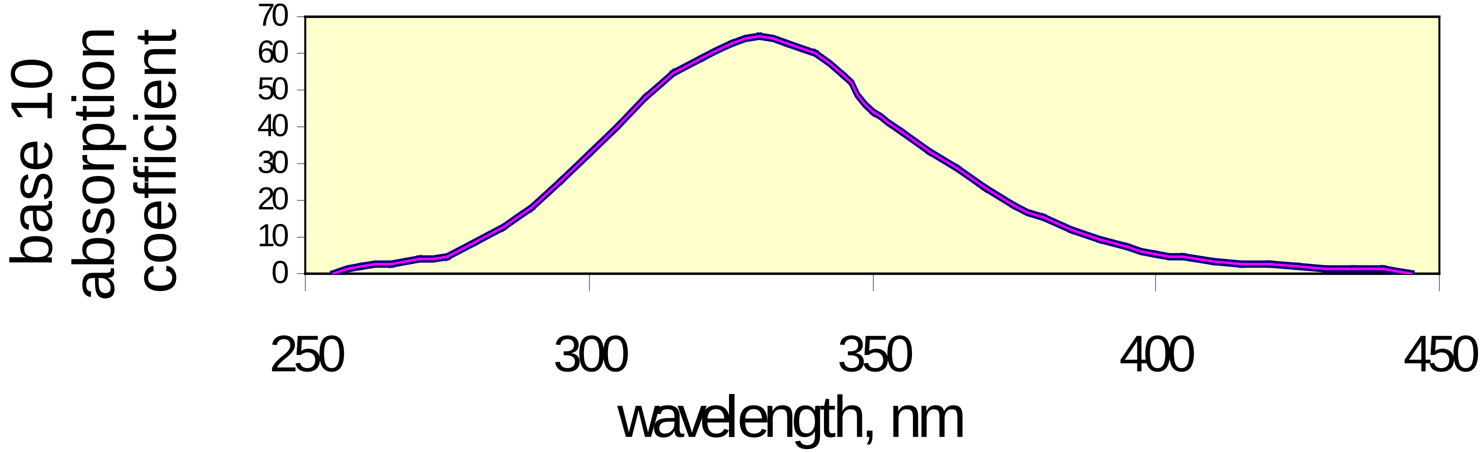
Benefits

- Eliminate aqueous cleans:
  - Reduced consumption of $HCl/H_2O_2/H_2O$
  - Less liquid waste
  - Conserve UPW
- Reduced worker exposure

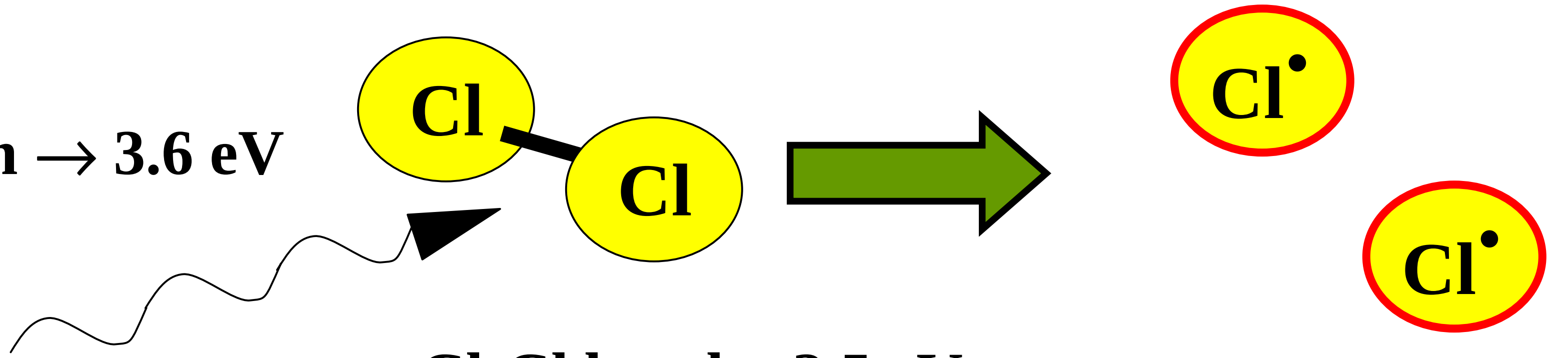
Concerns

- New kinds of waste
- Chlorine
- Ultraviolet exposure

Background Information—UV/Cl_2 Metal Removal



340 nm → 3.6 eV



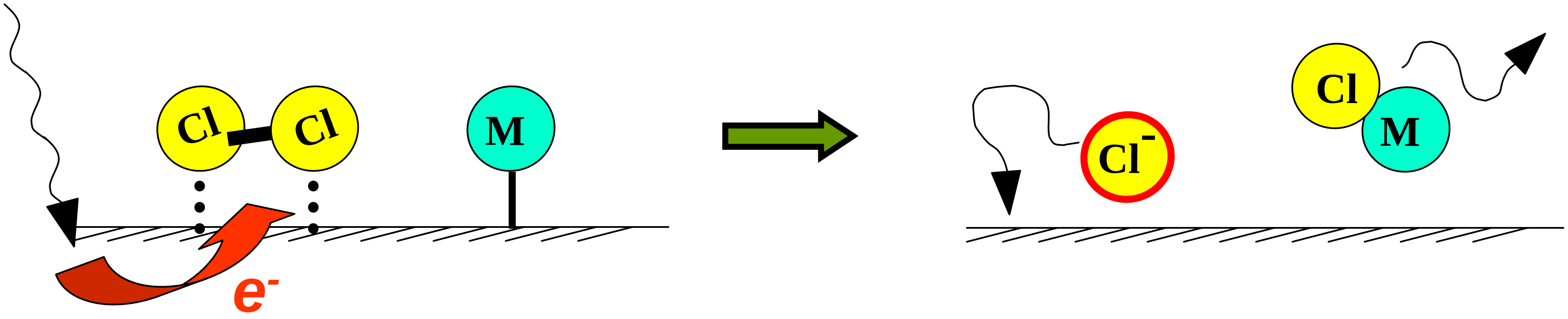
Cl-Cl bond = 2.5 eV

Project Objectives—UV/Cl_2 Metal Removal

- Verify UV/Cl_2 as clean
- Removal mechanism
  - "Lift-Off"
  - Volatile products
- Reaction mechanism and products
  - Gas-phase or surface photolysis
  - Substrate and dopants
  - Oxide thickness
  - Contaminant and its concentration
  - Surface termination and other adsorbed species
  - Ultraviolet wavelength
- Monochromatic UV source

Project Objectives—UV/Cl_2 Metal Removal

- UV-initiated surface reactions on Si and SiO_2.



- Relate electron-hole pairs to wavelength and dopant concentration.
- Model system for semiconductor/adsorbate/photon interactions.

International Technology Roadmap for Semiconductors

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 (white) — *Solutions Being Pursued* (yellow) — *No Known Solution* (red)

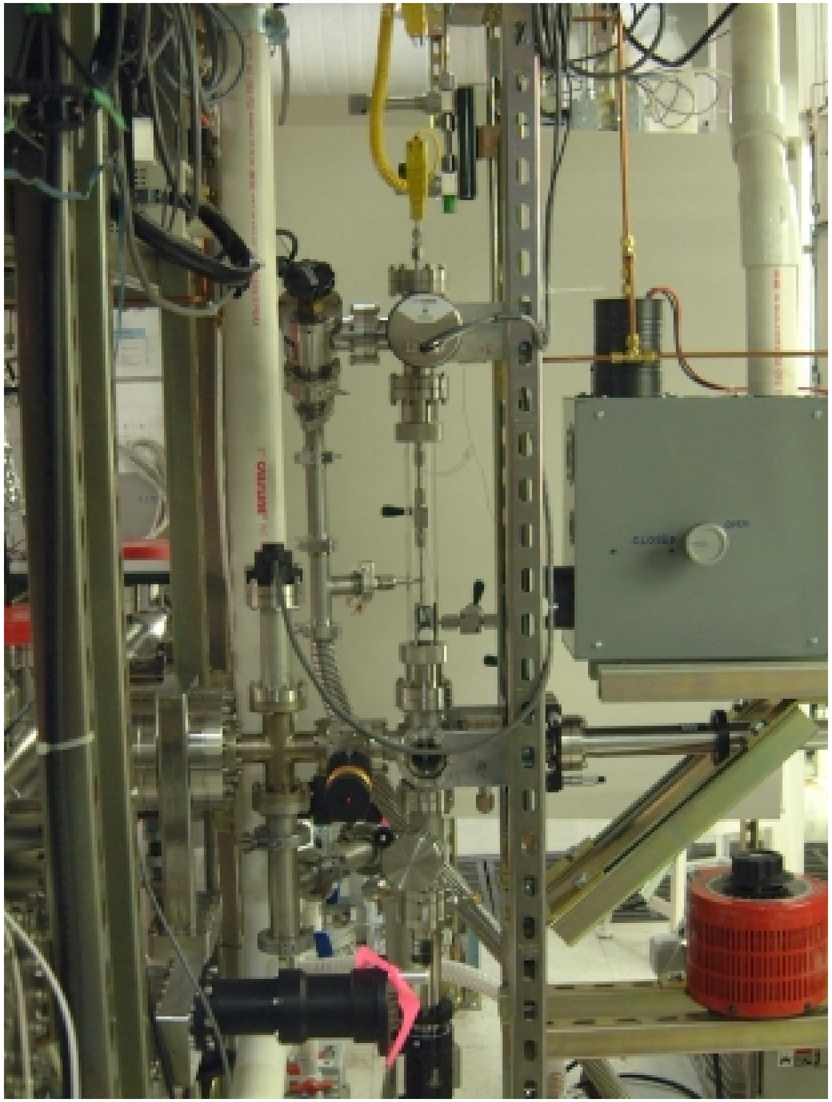
Critical Surface Metals: **Fe[1,4],Ca, Co, Cu[1,3,4], Cr, K[1], Mo, Mn, Na[1], and Ni[1,2,4]**

1. Sugino, et al.   2. Courtney and Lamb   3.Opila, et al.   4. Lawing, et al.

Thermochemistry

Reaction	ΔG_{rxn} (250°C)	P_{sub} (250°C)
$Cu + Cl(g) \rightarrow CuCl$	-219 kJ/mol	$4x10^{-5}$ Torr
$Cu + 2Cl(g) \rightarrow CuCl_2$	-322 kJ/mol	$4x10^{-7}$ Torr
$Cu_2O + 2Cl(g) \rightarrow 2CuCl + ½ O_2(g)$	-307 kJ/mol	$4x10^{-5}$ Torr
$CuO + Cl(g) \rightarrow CuCl + ½ O_2(g)$	-112 kJ/mol	$4x10^{-5}$ Torr

UV Reactor Schematics



Present Reactor

- Temperature (100 - 250^{o}C) and pressure (25 - 500 mTorr) controlled
- 15 - 50 sccm Cl_2 flowrate
- 250-Watt Hg arc lamp

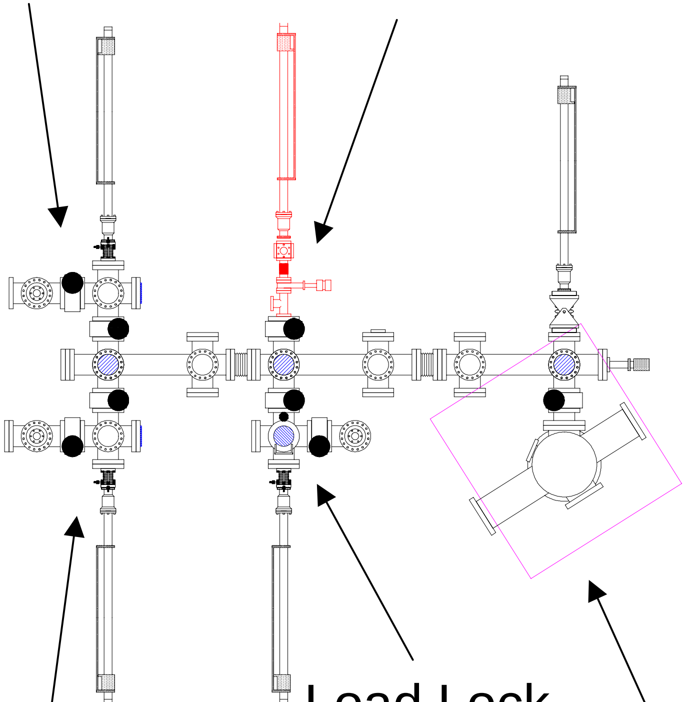
Future Reactor

- *In-situ* Fourier Transform Infrared Spectroscopy (FTIR)

Integrated Processing Apparatus

UHV SSC reactor

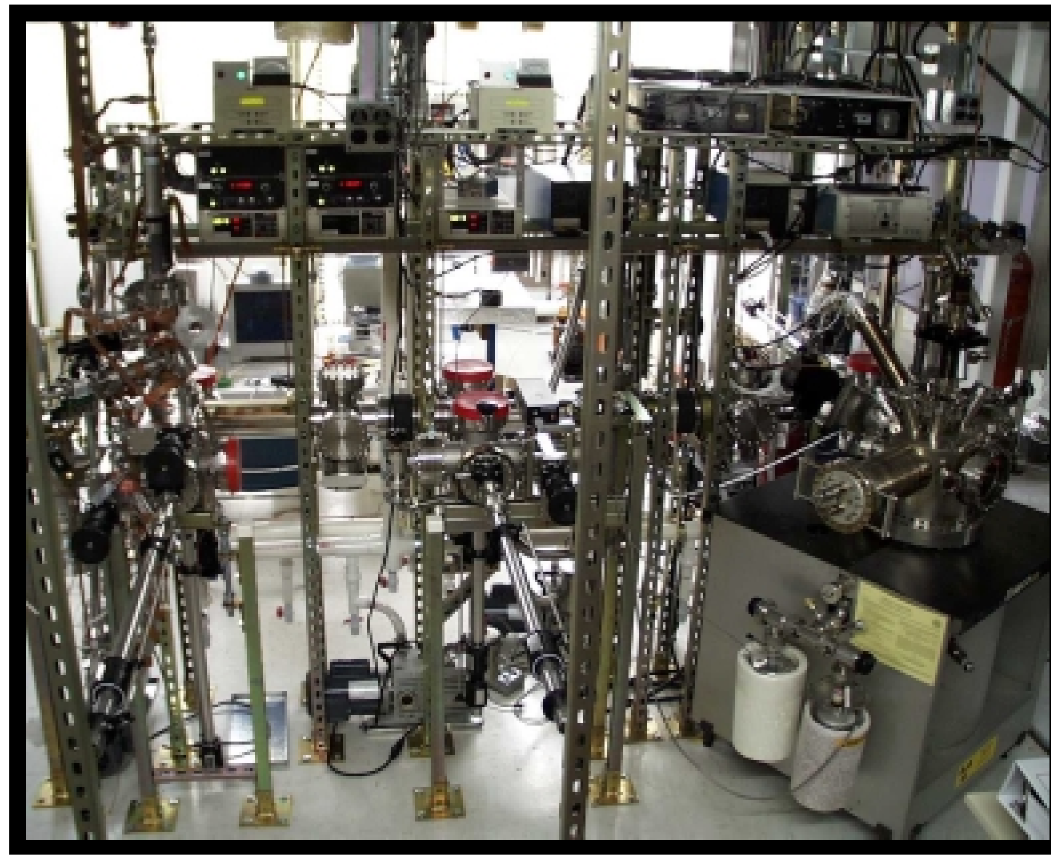
UV/Cl_2 reactor



Load Lock

HF/Vapor Phase Etching Reactor

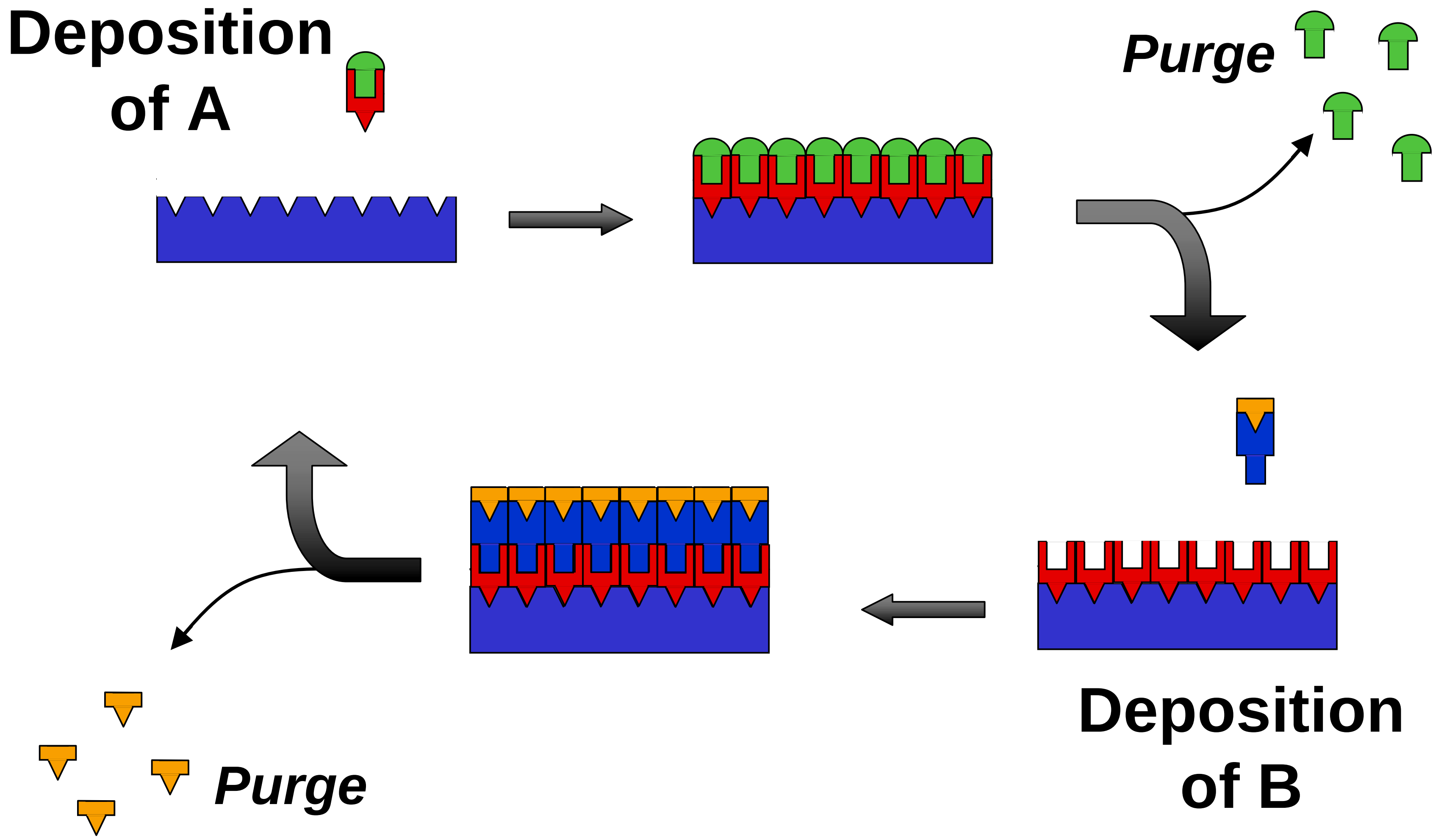
Ultra High Vacuum Surface Analysis Chamber



Outline

- UV-initiated surface preparation
  - UV/Cl_2 metals removal
- Experimental Setup
- UV-initiated surface reactions
  - UV-enhanced Atomic Layer Deposition (ALD)
- Summary

Schematic of Atomic Layer Deposition



UV Atomic Layer Deposition

Thermal ALD

- 1/10th of a layer per cycle
- High temperature Process
  - 500^{o}C
  - processing conflicts
- Pulse and Purge

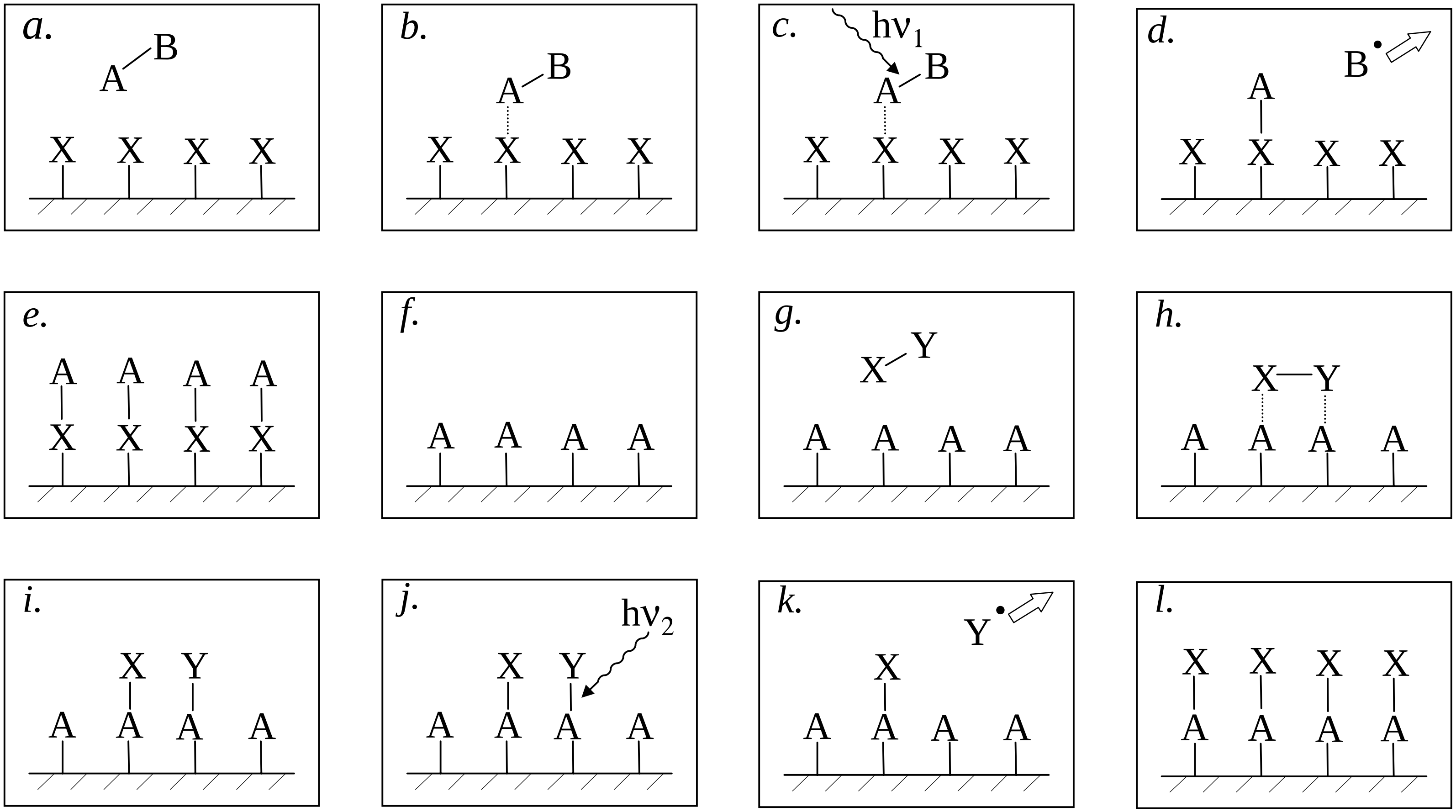
UV ALD

- 1 layer per cycle
  - Improved deposition rate
- Lower temperature
  - High-K dielectric layers, Diffusion barriers
- Reaction triggered by UV illumination.
  - Eliminate pulse-purge cycles
  - Decrease consumption

Project Objectives — UV Atomic Layer Deposition

- Precursor sequences for deposition of ZrO_2
- Reduced processing temperatures
- Mechanisms and kinetic parameters
- Multiple precursors simultaneously
- Resist-free patterning

Possible UV-Enhanced Deposition Sequence



Summary

UV/Cl_2 Metal Removal

- Nickel, copper, iron, sodium, potassium and organic contaminants
- Reaction and removal mechanisms
- Monochromatic light source

UV-Enhanced Atomic Layer Deposition

- Identify and test precursor combinations
- Grow high quality, commercially useful films at low temperature
- Both precursors present simultaneously

Acknowledgements

- Anthony Muscat, Kasi Kiehlbaugh, Gerardo Montaño, Adam Thorseness
- Bob Opila, Lucent Technologies
- Scott Lawing, Rodel
- SRC Graduate Fellowship (C. Finstad)
- Air Products for donation of chlorine gas and regulator
- SRC/NSF Environmentally Benign Semiconductor Manufacturing Center
- NSF Career Award (DMR-9703237)