Investigation of Copper Impurities on Silicon Surfaces using X-ray Absorption Near Edge Spectroscopy and Total Reflection X-ray Fluorescence

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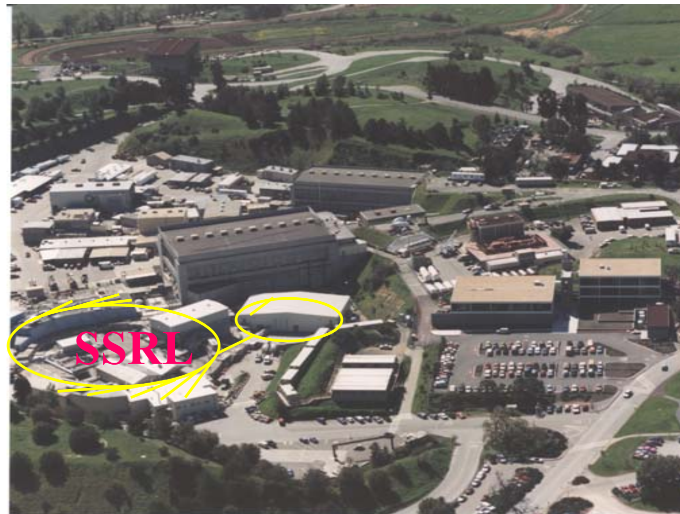


Funded by Department of Energy, SIWEDS

Motivation: Why Cu on Silicon?

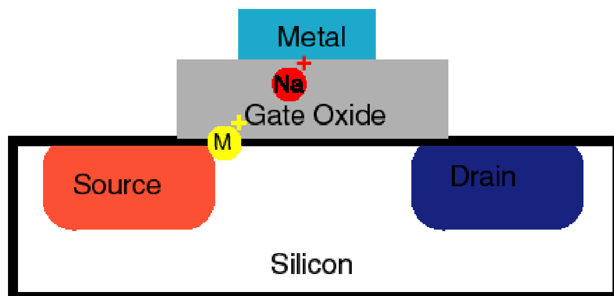
SSRL

Device degradation

•Cu recently introduced for interconnects

•Cu is a fast diffuser in Silicon

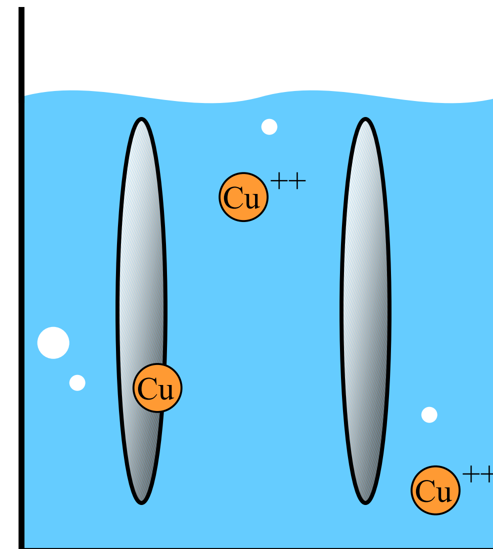
•Contamination Levels ~ 10^9 atoms/cm^2



Electrochemistry

•Understand electrochemical nucleation and growth

•Improve silicon cleaning technology



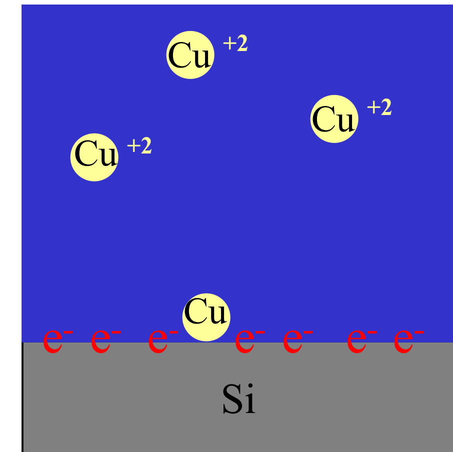
Reaction pathways

SSRL

Low pH - reductive

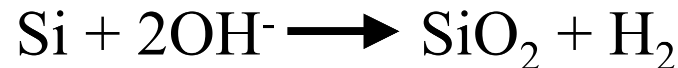
$$Cu^{2+} + e^-_{Si} \longrightarrow Cu^{1+}$$

$$Cu^{1+} + e^-_{Si} \longrightarrow Cu^{0}$$

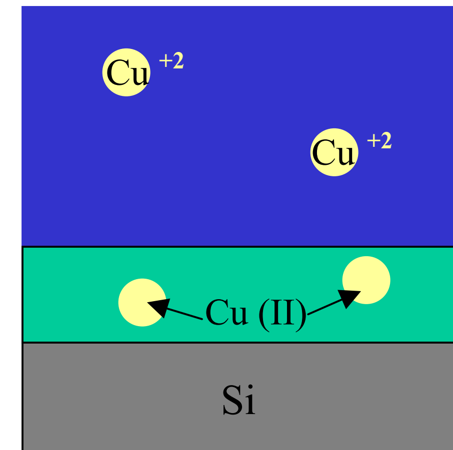


Metallic clusters

High pH - oxidative



$$Si + 2OH^- \longrightarrow SiO_2 + H_2$$

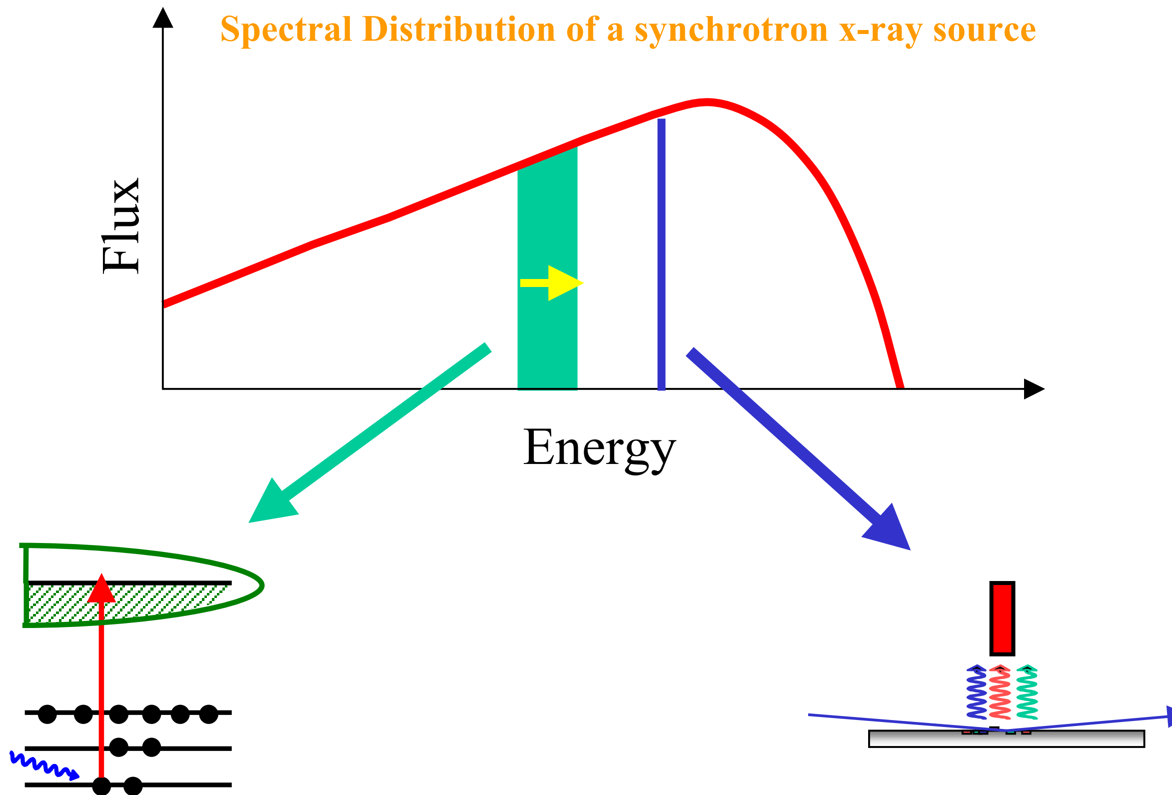


Metal incorporated into oxide

In ultra pure water (UPW)?

- Deposition influenced by **O_2 content**, light, defects, etc.

Silicon Wafer surface analysis techniques



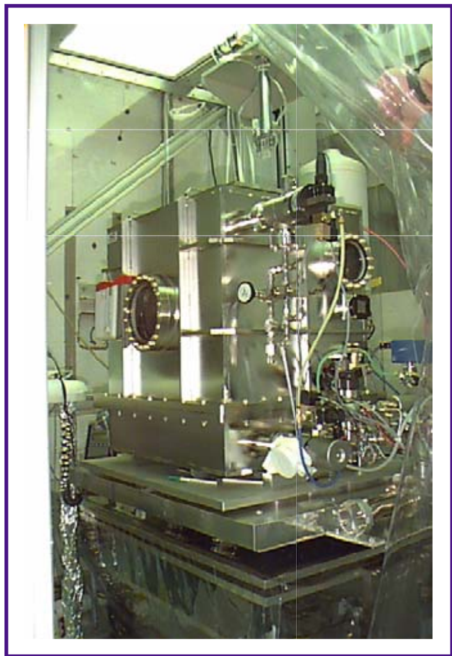
X-ray absorption Near Edge Spectroscopy (XANES)

- Incident beam energy scanned through an absorption edge of interest
- Determines chemical state (i.e. oxidation state) of impurities

Total Reflection X-ray Fluorescence (TXRF)

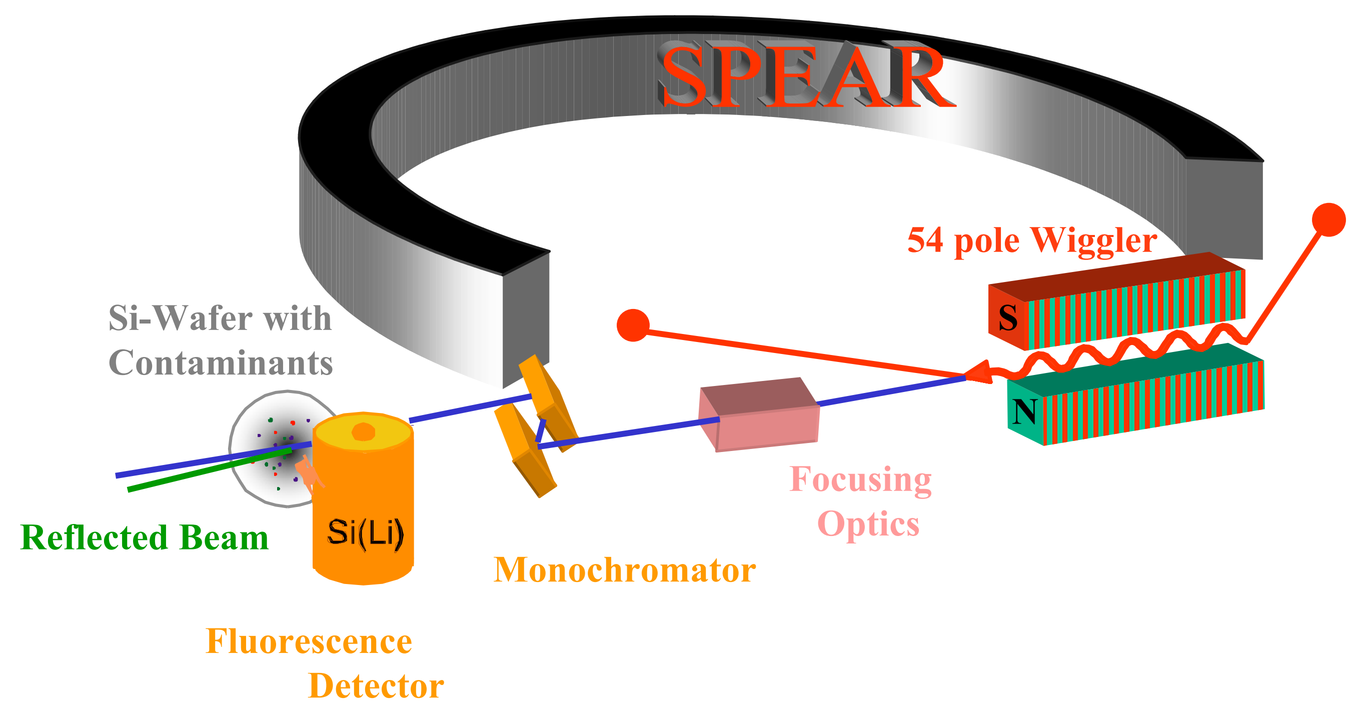
- Incident beam at constant energy
- Useful for determining concentration
- Angle scans can probe location of impurities

Experimental setup at SSRL

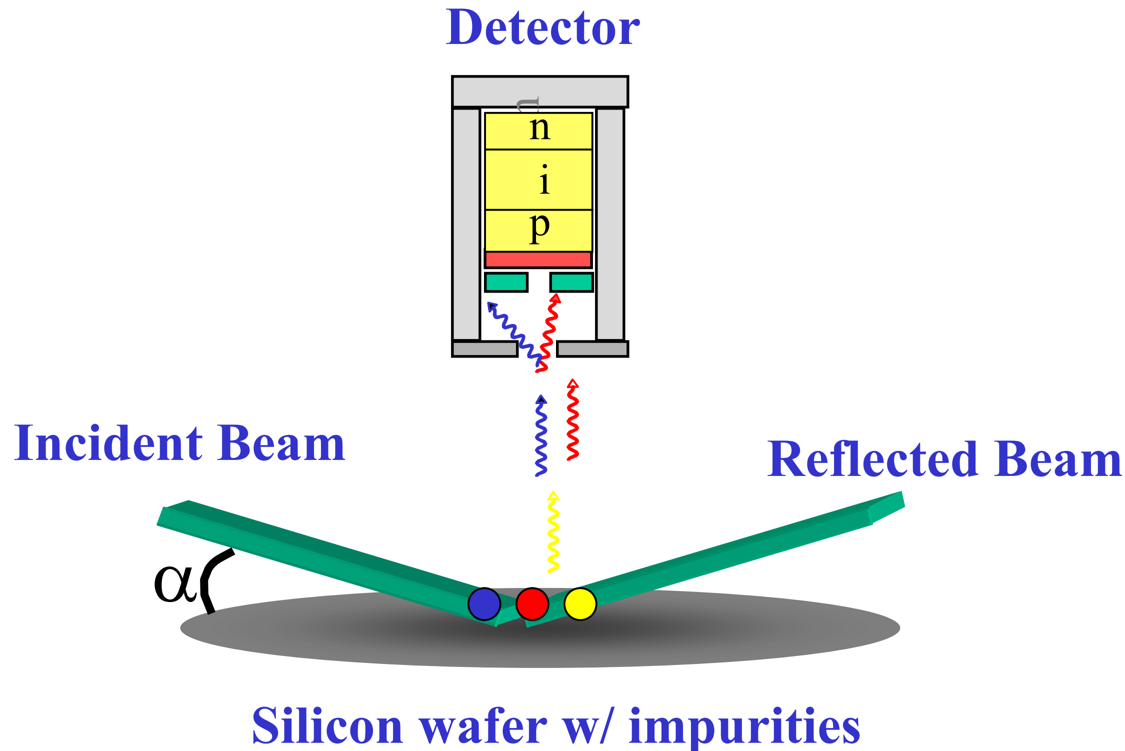


TXRF end station at BL 6.2

Wafer handling robot



Total Reflection X-ray Fluorescence



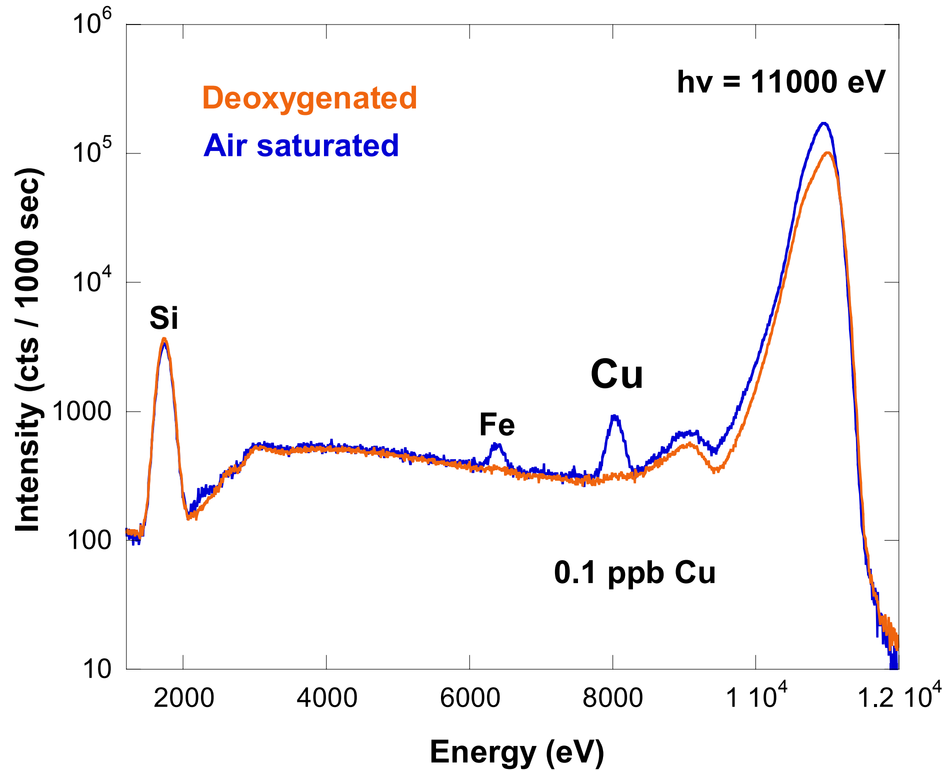
- Grazing incidence geometry (α ~ .10 degrees)
- High surface sensitivity (30 angstroms)
- Determines **concentration** of impurities
- Detection Limit is 8E7 atoms/cm^2 (i.e. 1 atom in 10 million)

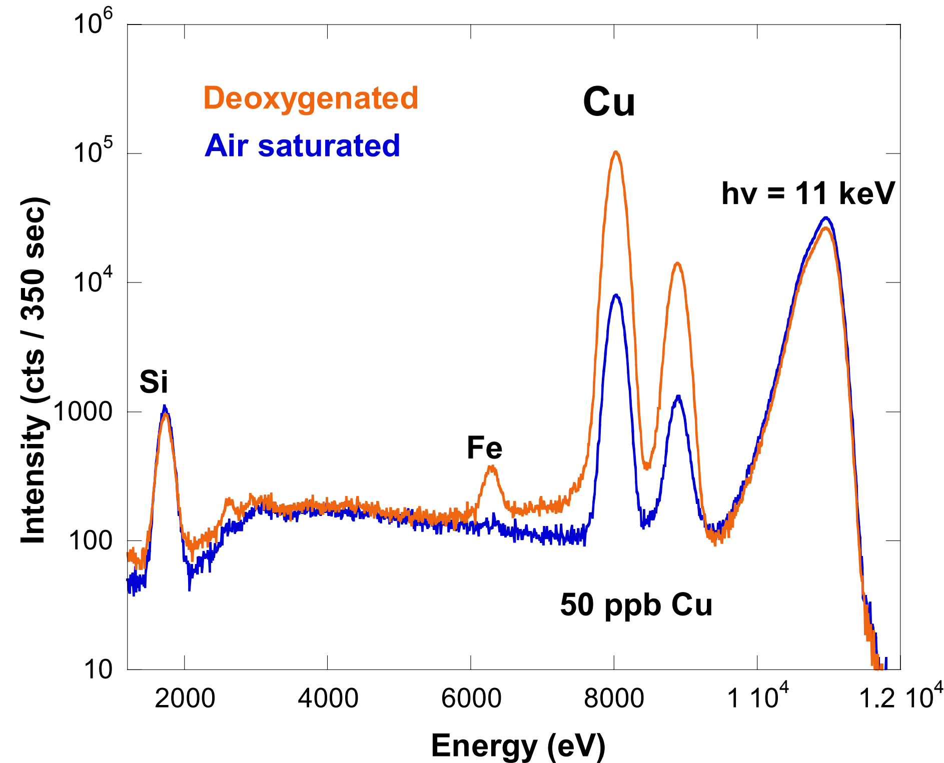
Sample preparation

SSRL

Wafer:	p-type Si (100) (9-18 Ωcm)
Pre-cleaning:	$H_2SO_4 : H_2O_2 = 4:1$ (120^0C, 10 min)
	0.5% HF (1min)
Metal source:	$Cu(NO_3)_2$ (10 ppt → 500 ppb)
Ultra Pure Water:	Milli – Q (18 MΩ)
Dissolved oxygen control:	UPW_{deox}: 0.3 ppm
	UPW: 3.4 ppm

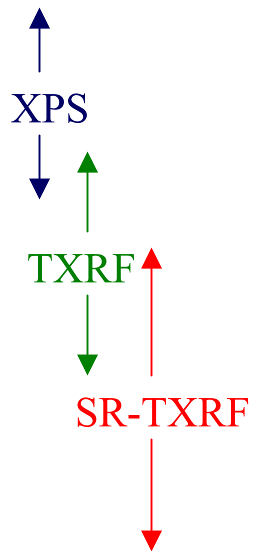
Effect of dissolved oxygen on Cu deposition





- Background consists of scatter in the high energy region and bremsstrahlung in the low energy region
- Concentration determined with a known standard

Trace contamination from Cu spiked UPW



500 nm

Deoxygenated

Air saturated

Deposited amount (atoms/cm^2)

1.00E+16
1.00E+14
1.00E+12
1.00E+10
1.00E+08
1.00E+06

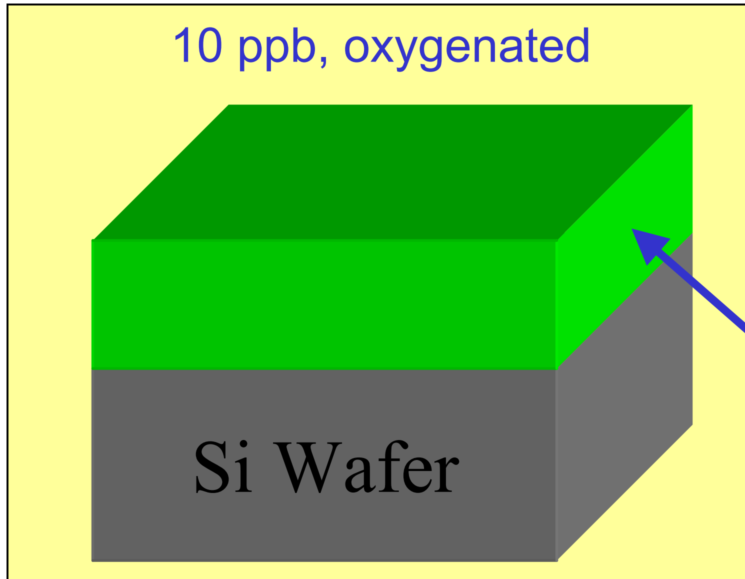
0.001 0.01 0.1 1 10 100 1000

Cu concentration / ppb

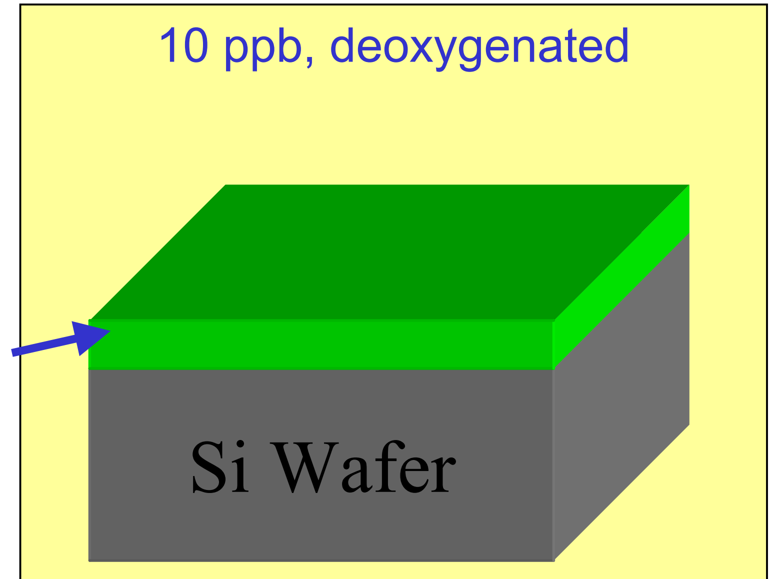
500 nm

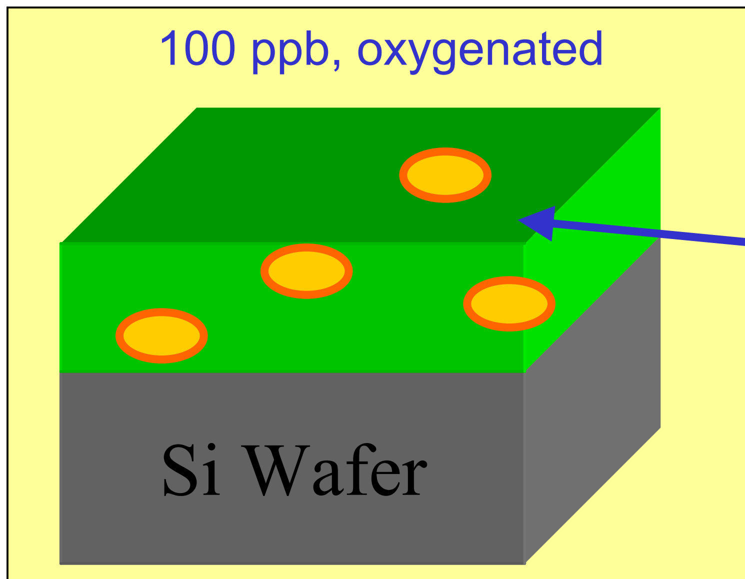
*After 5 min immersion

Schematic model for Cu species on Si Wafer

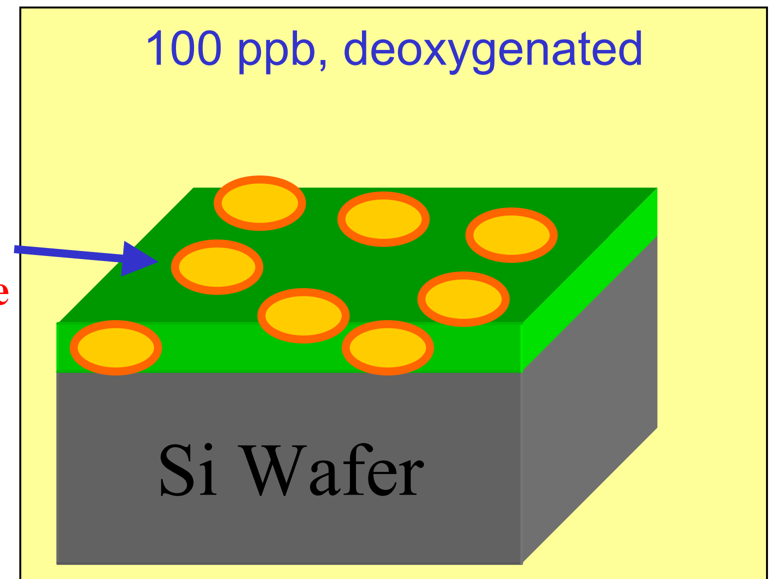


Surface oxide containing Cu oxide species

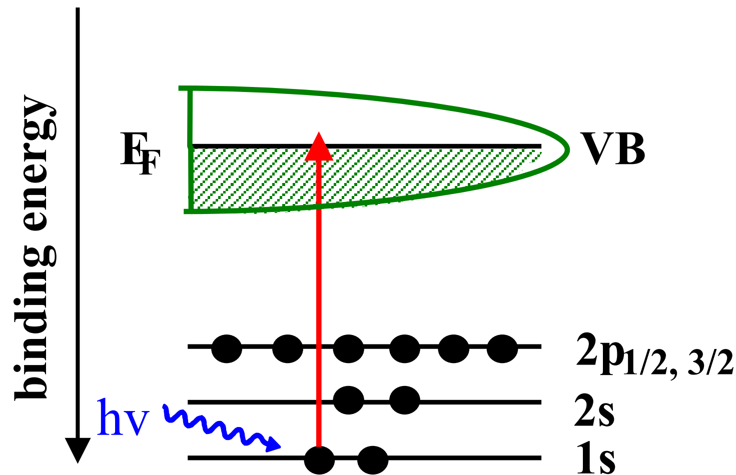


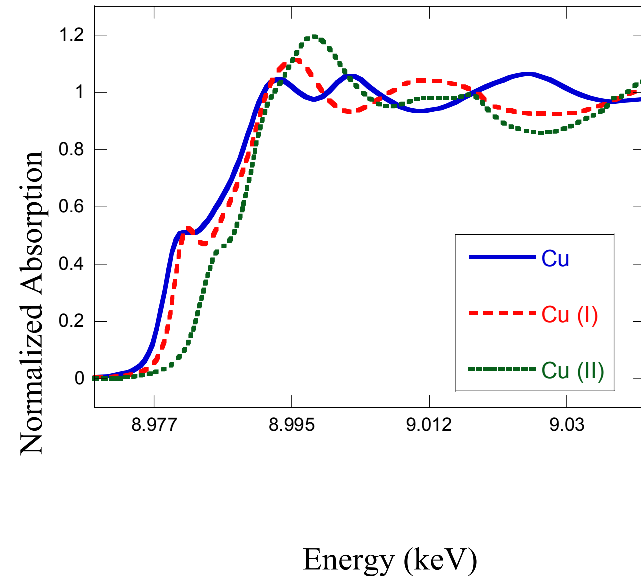


Cu metallic particle with "native" surface oxide



X-ray absorption Spectroscopy (XANES)





- Feasibility due to broadband nature of synchrotron radiation
- Low concentrated samples can be measured (detection limit ~ 1E10 atoms/cm^2)
- Edge position can identify oxidation state
- Near edge structure probes electronic structure
- SR-TXRF setup is used → Fluorescence Detector measures absorption
- Theoretical predictions difficult, but possible with FEFF8

Copper reference samples

Cu

Cu_2O

CuO

Normalized Absorption

1.2
1
0.8
0.6
0.4
0.2
0

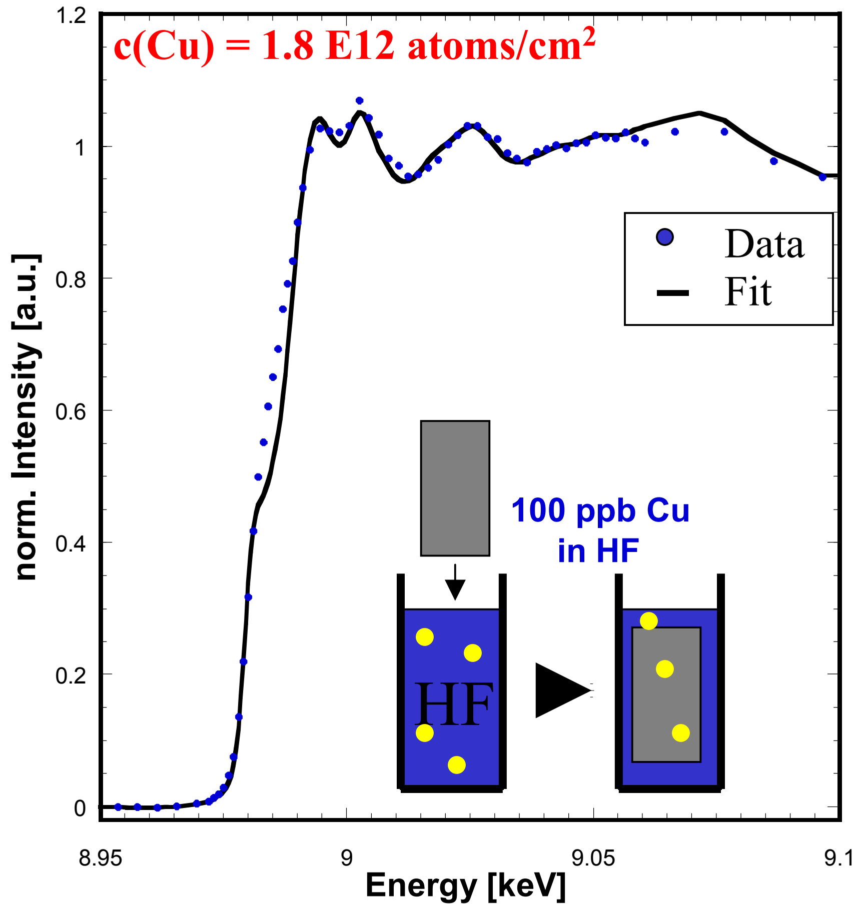
8.96 8.98 9 9.02 9.04 9.06

Energy (keV)

1.2
1
0.8
0.6
0.4
0.2
0

8.97 8.975 8.98 8.985 8.99 8.995 9

Proof of Principle: 100 ppb Cu in HF



Predominantly Cu metal

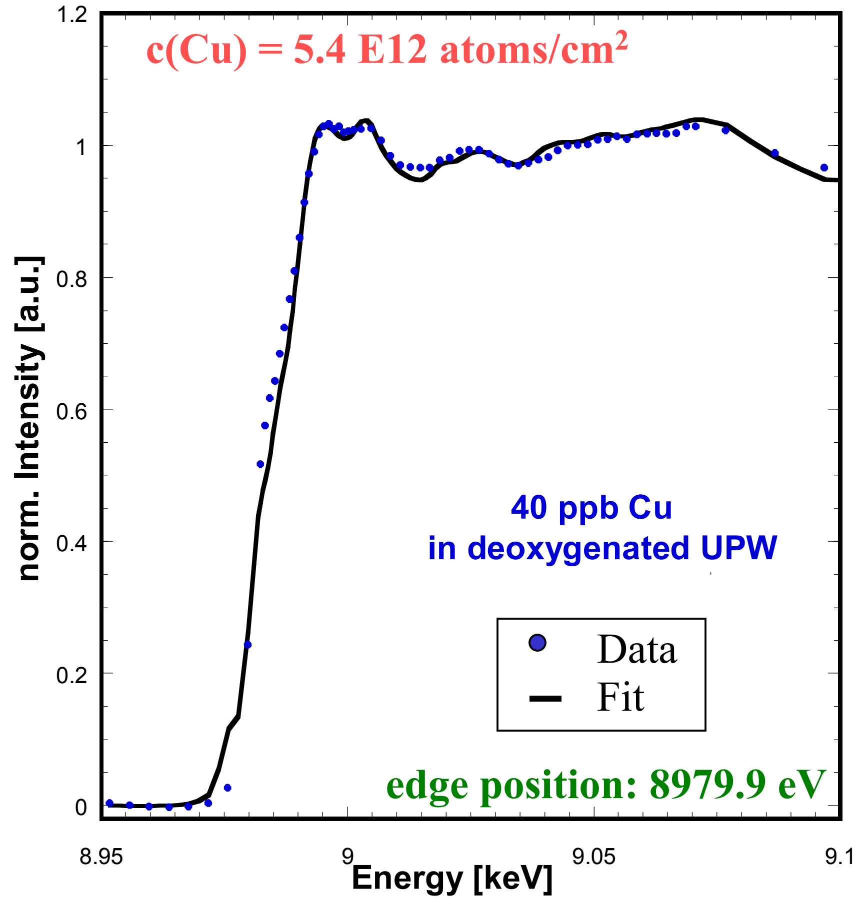
Cu	(0):	78%
CuO	(II):	17%
Cu2O	(I):	5%

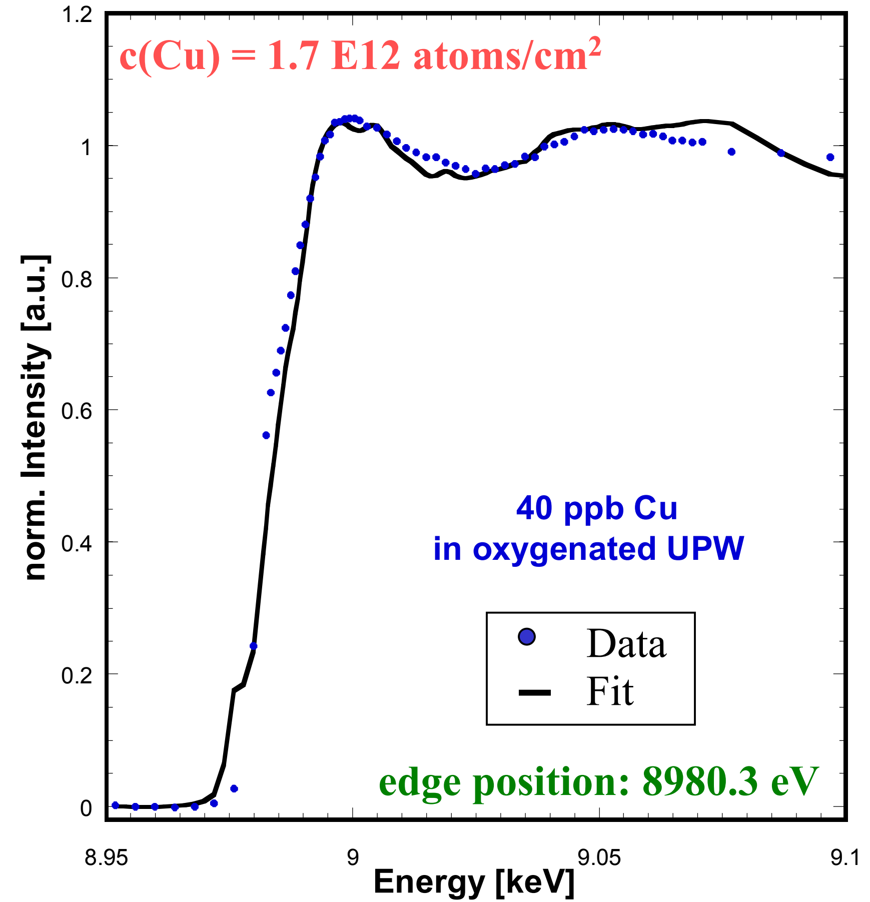
reductive deposition:

$$Cu^{2+} + e^{-}_{Si} \longrightarrow Cu^{1+}$$

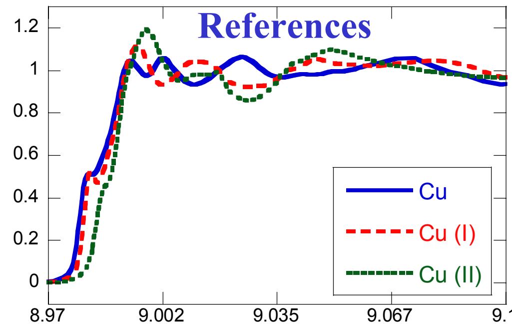
$$Cu^{1+} + e^{-}_{Si} \longrightarrow Cu^{0}$$

40 ppb Cu in UPW



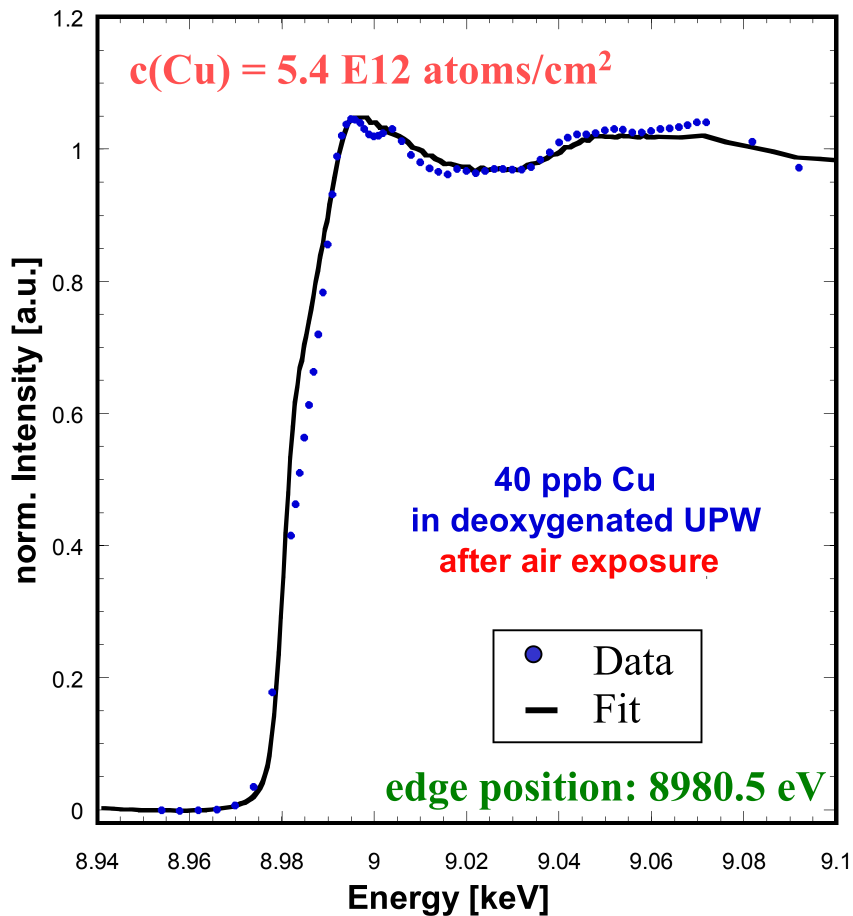


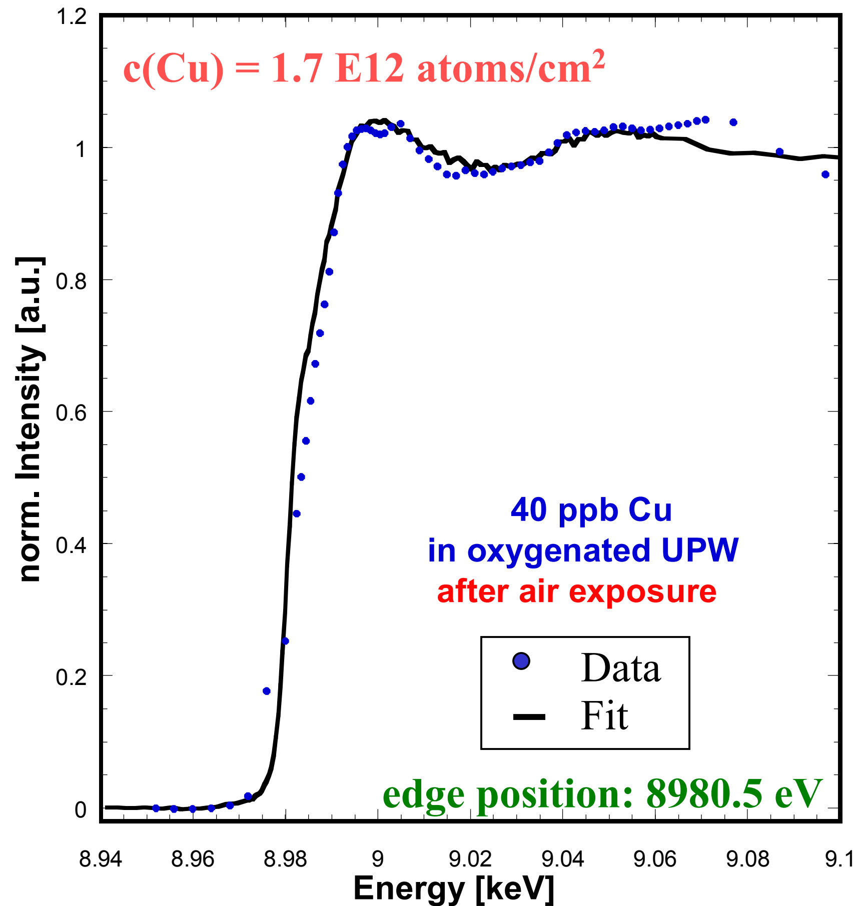
Cu (0) : 60%
Cu (I) : 19%
Cu (II): 21%



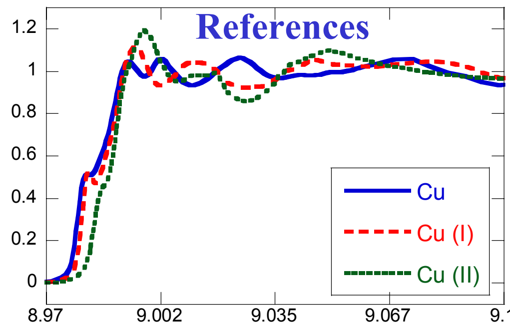
Cu (0) : 38%
Cu (I) : 34%
Cu (II): 28%

40 ppb Cu in UPW, after Air Exposure





Cu (0) : 46%
Cu (I) : 26%
Cu (II): 28%

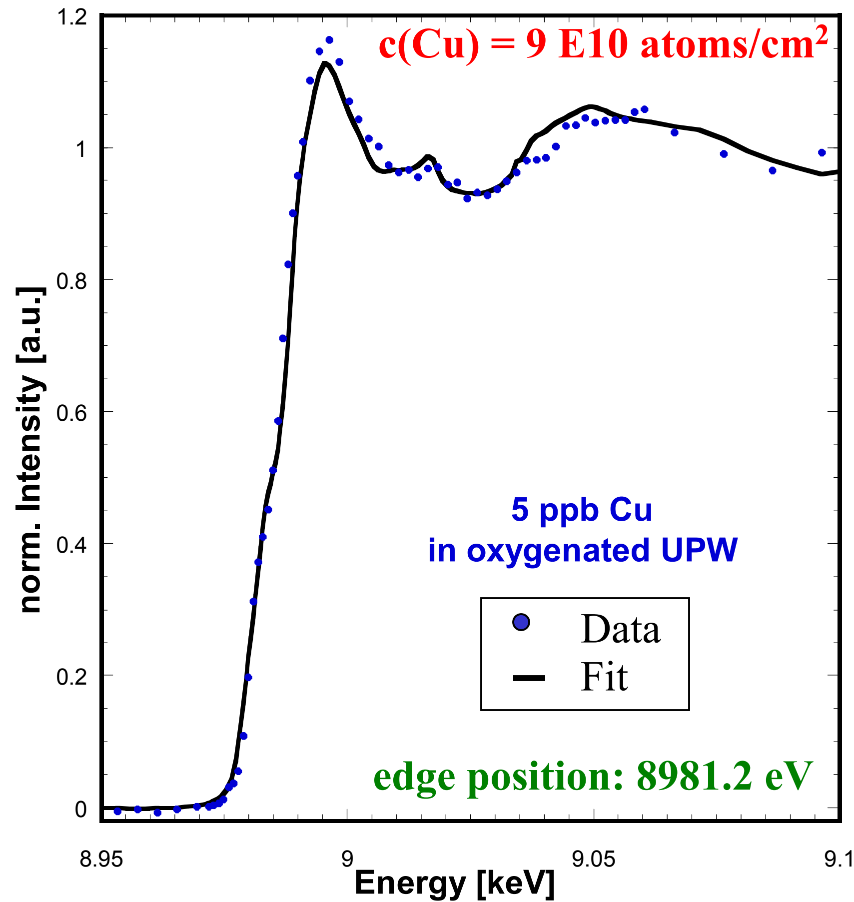


Cu (0) : 39%
Cu (I) : 35%
Cu (II): 26%

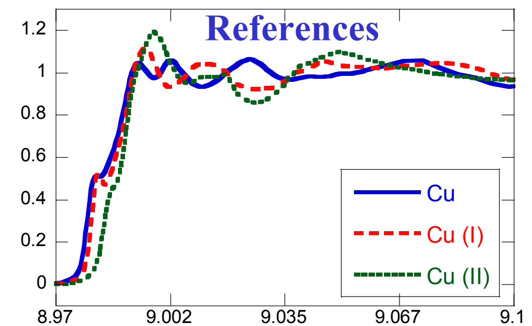
⟹ stable in air

Below the critical concentration: 5 ppb Cu in UPW

first results:



Cu (0): 35%
CuO (II): 65%



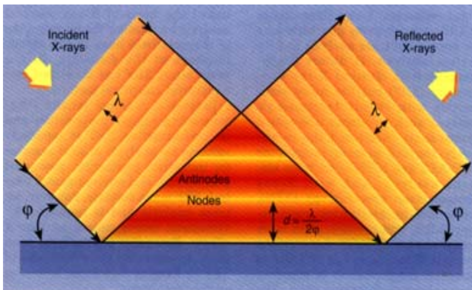
Variation of the angle of incidence

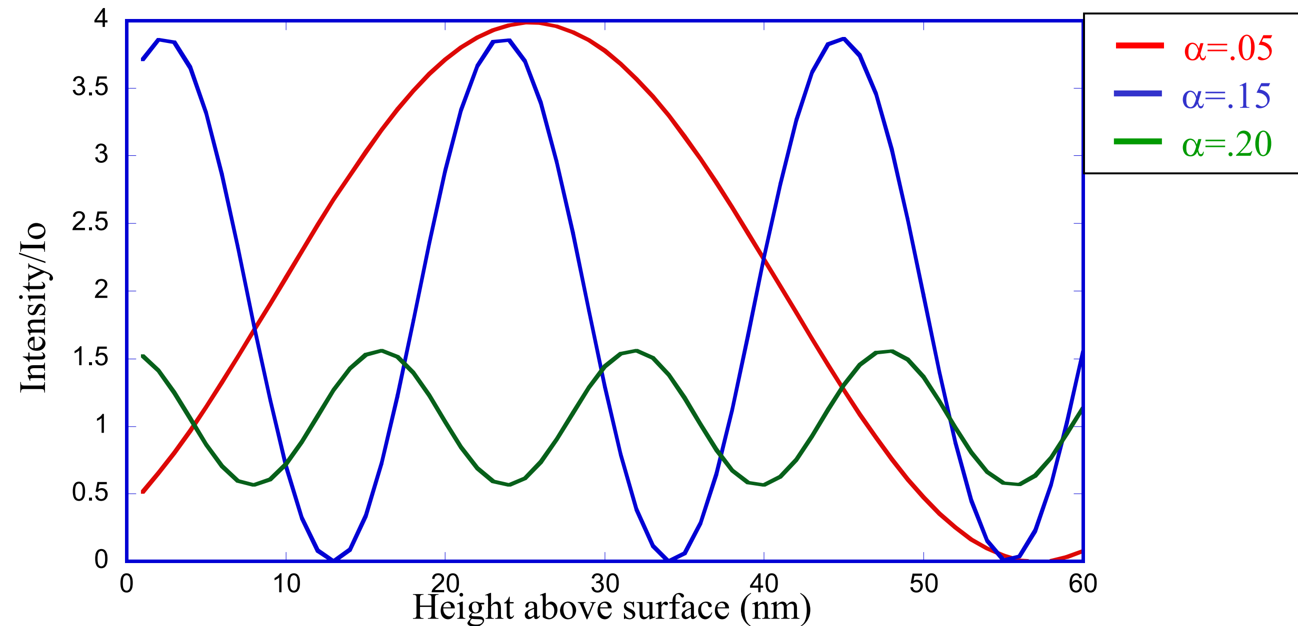
$$I(\alpha,z)=I_o*[1+R(\alpha)+2\sqrt{R(\alpha)}*\cos[\frac{2\pi\cdot z}{d}-\phi(\alpha)]$$

Φ : phase shift due to total external reflection

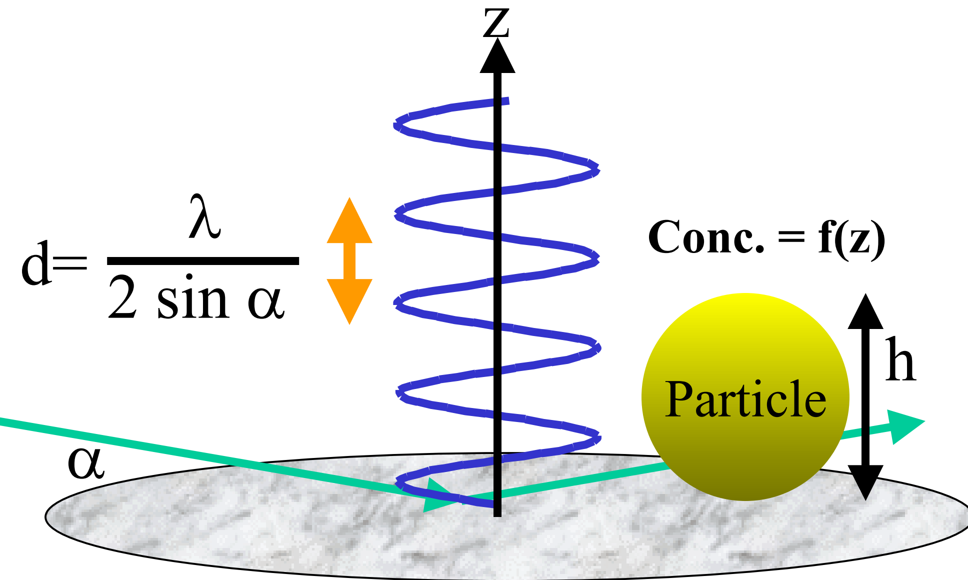
R(α) : reflectivity

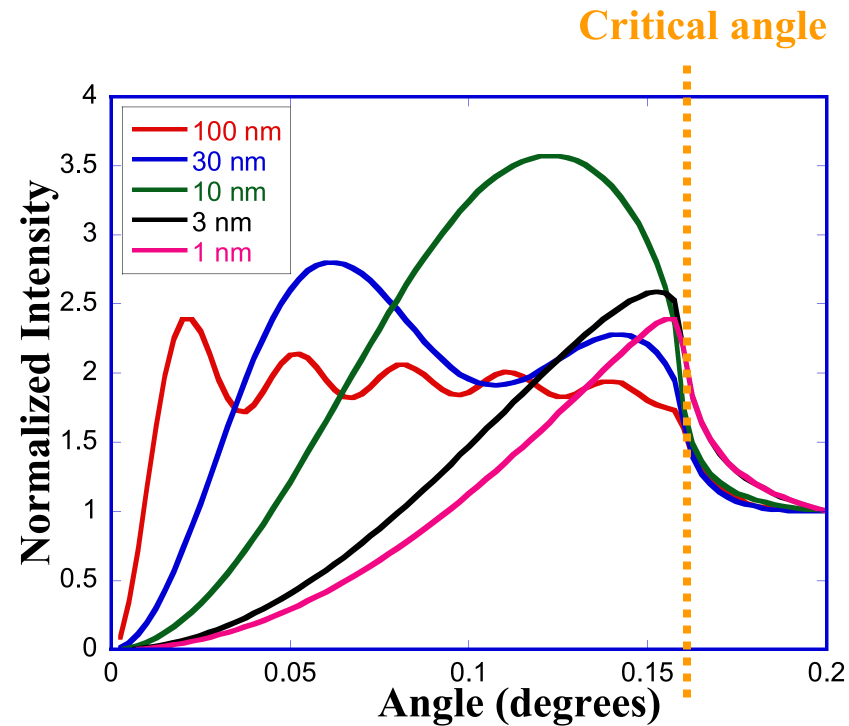
d = λ/2sinα





Variation of the angle of incidence

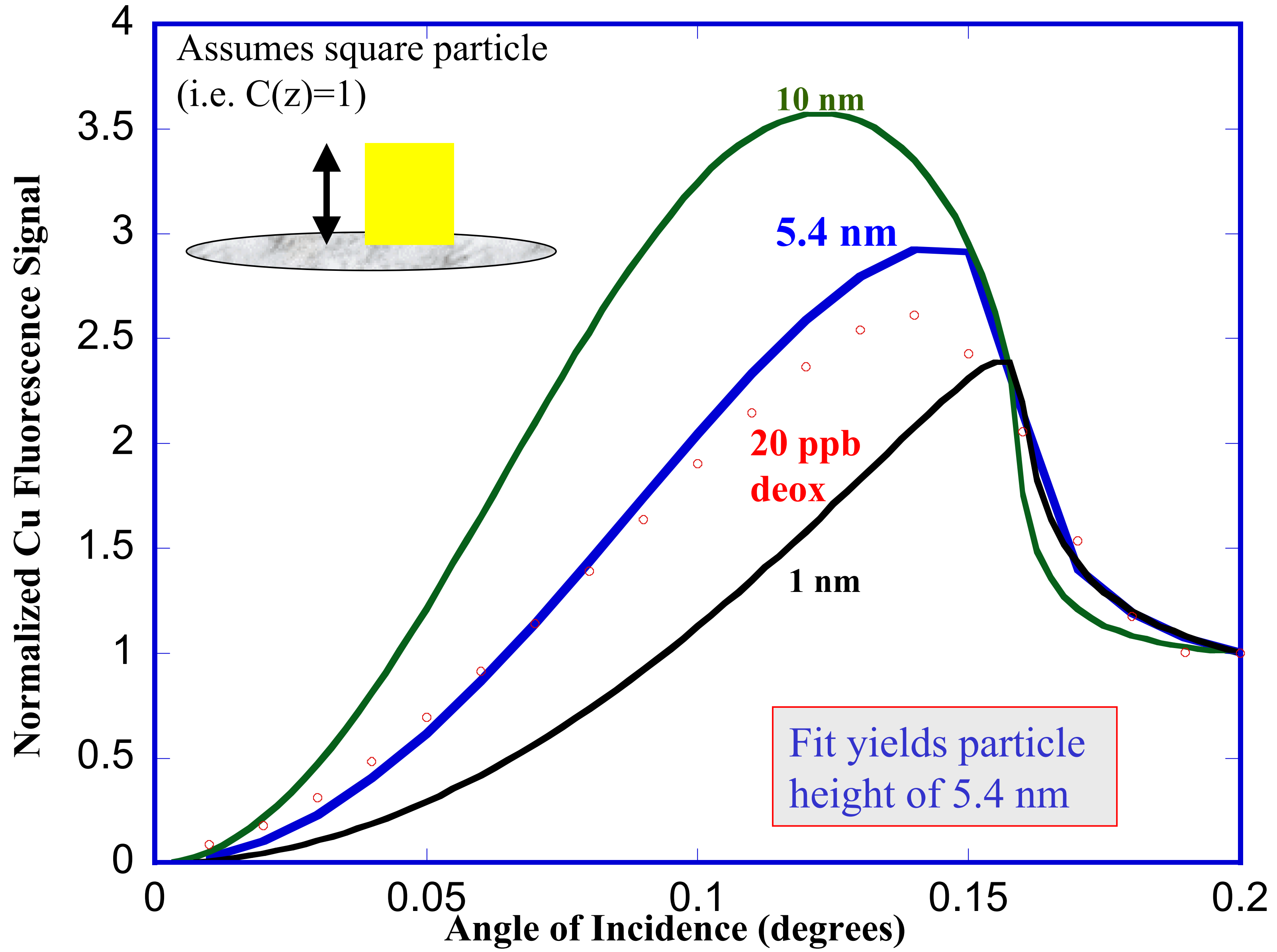




$$Fluorescence \propto \int_0^h I(z) * C(z) * dz$$

- Standing waves formed at glancing angles below critical angle
- Periodicity of SW modulated by angle

Determination of the particle size



Summary/Outlook

Summary

Deoxygenated UPW	Air-saturated UPW
•Predominantly, Cu metal deposition •Oxidation in air •Particle growth seen by AFM, angle scans	•Deposition of Cu metal and oxides •Samples are stable in air

Outlook

•XANES at lower concentrations → below "flipping point"
•In-situ experiment to remove environmental contamination
•Nucleation & growth experiments - particle size/conc. as a f(time)