

# Surface X-ray Diffraction Characterization of Corrosion Products

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# Important Contributions from:

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- Andy Gewirth                University of Illinois
- Sébastien Boutet             University of Illinois
- Don Walko                     University of Illinois
- Nancy Missert                Sandia National Lab

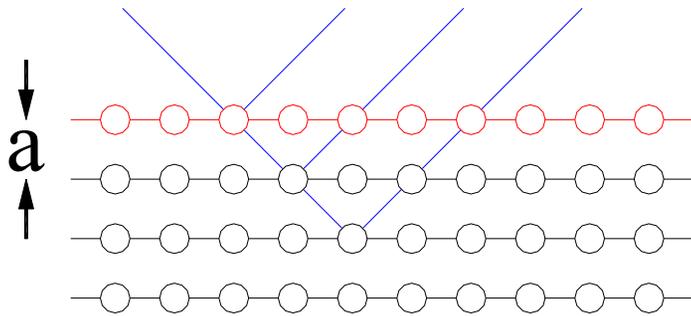
# Talk Outline

- Interfacial Diffraction Methods
- Crystalline Oxides
- “Amorphous” Oxides
- Identification of Corrosion Products
- Future Developments

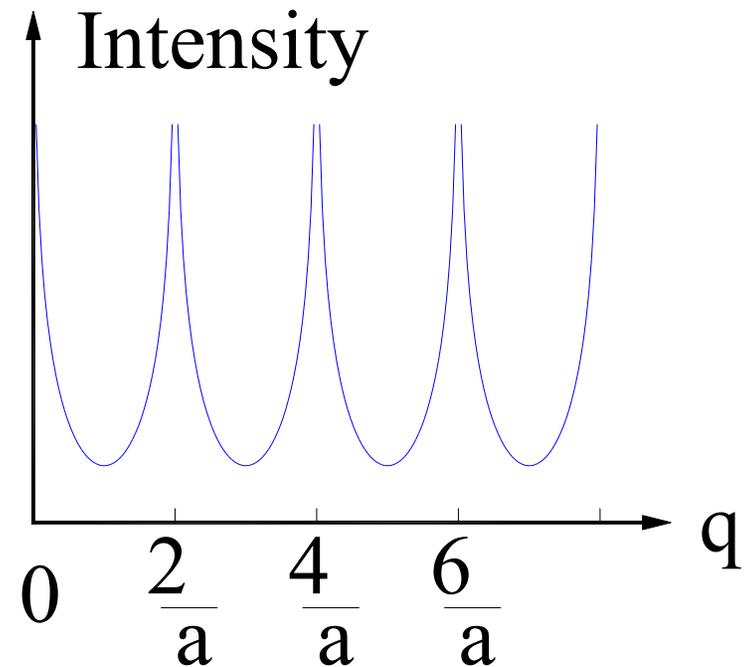
# Crystalline Oxides

- Penetration of X-rays: *in-situ* methods
- Crystal Truncation Rods
- Interface Sensitivity is due to Symmetry
- Detailed Structural Information
  - Bondlengths to 0.02Å
  - Site Occupancies
  - Strains down to 0.1%
- Methods Limited to Epitaxial Crystalline Overlayers

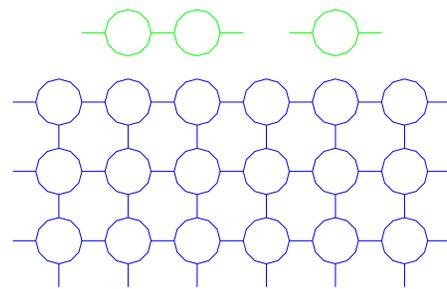
# Crystal Truncation Rods



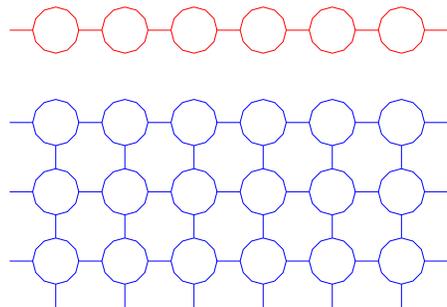
$$\begin{aligned} F_{CTR} &= \sum_{n=0}^{\infty} A_n \\ &= \sum_{n=0}^{\infty} f_L e^{inqa} \\ &= \frac{f_L}{1 - e^{iqa}} \end{aligned}$$



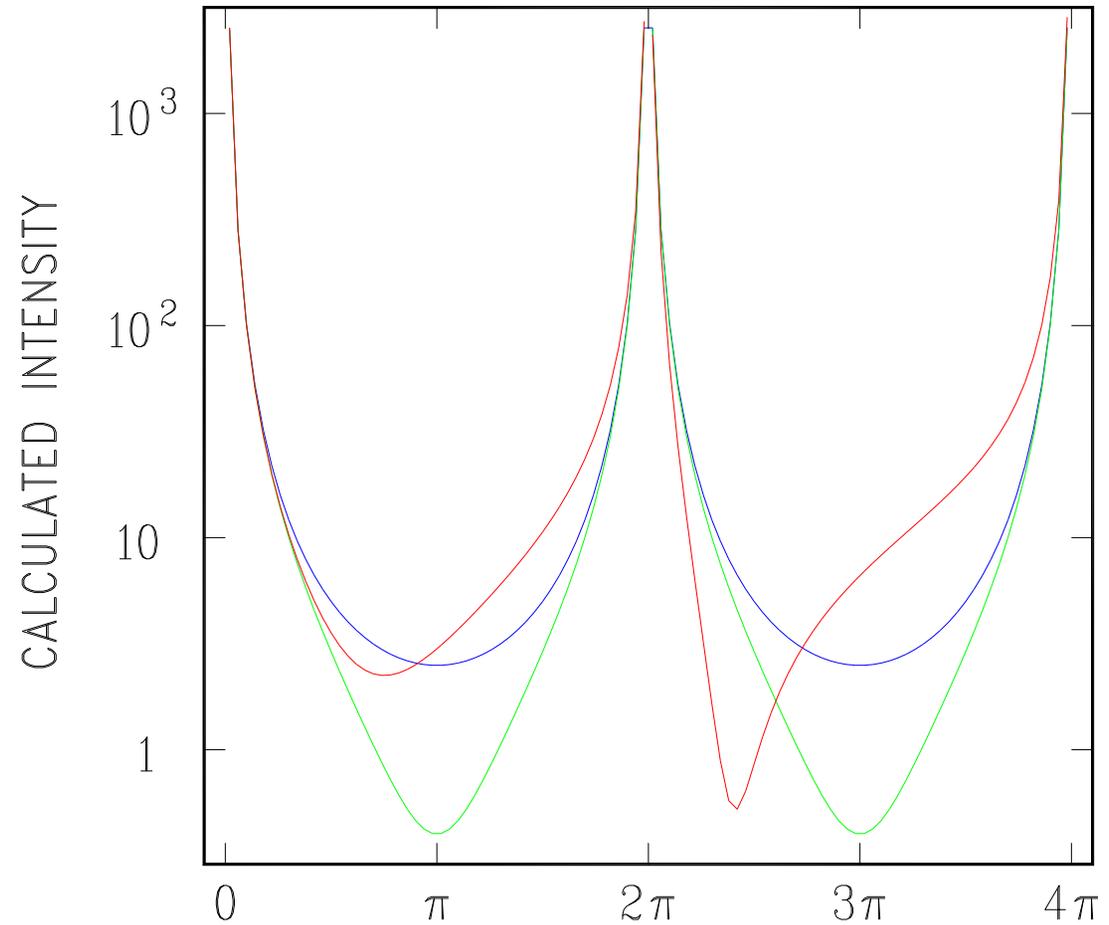
# CTR is Sensitive to Surface Structure



ROUGH SURFACE

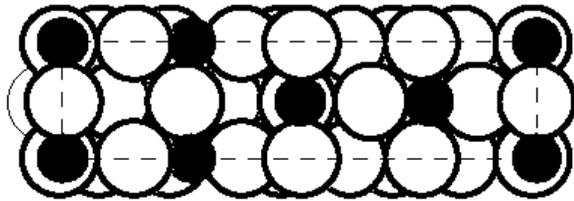


EXPANDED LAYER

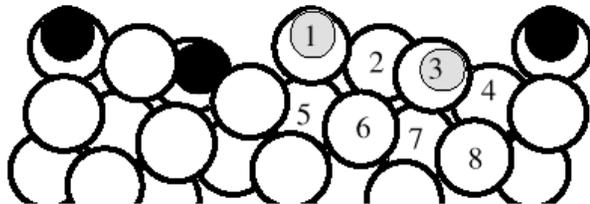


# Simple CTR Example: O/Cu(104)

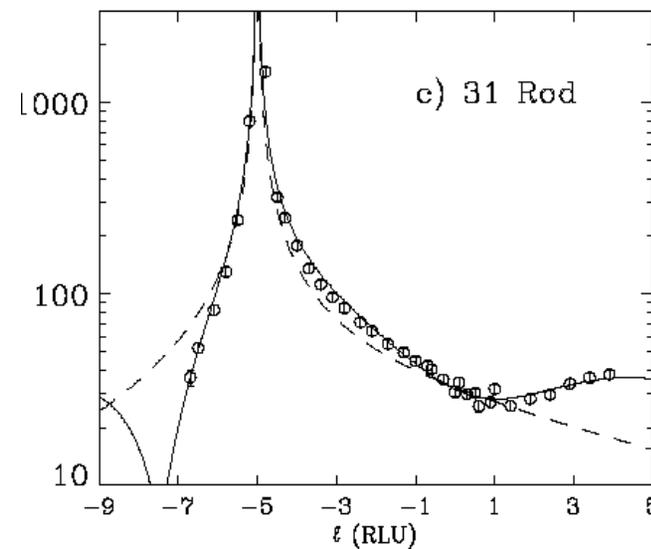
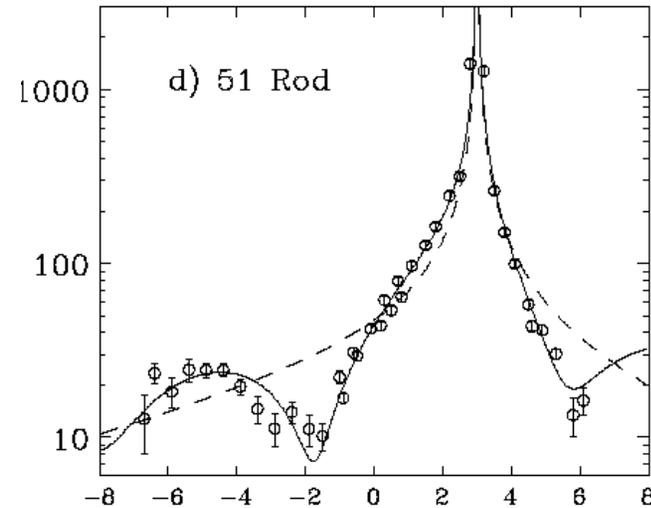
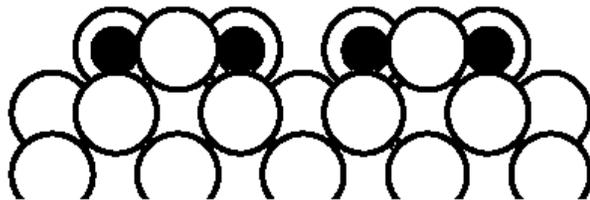
a) top view: O/Cu(104)



b) side view: O/Cu(104)

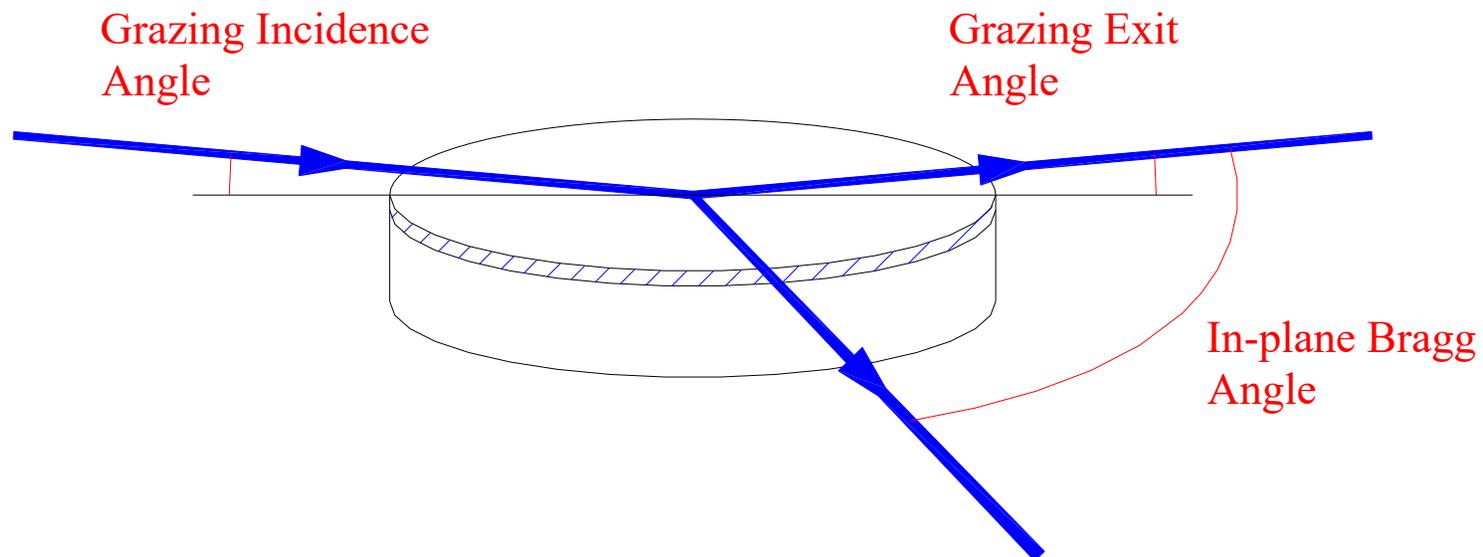


c) side view: O/Cu(001)(2√2×√2)



# Grazing Incidence Diffraction

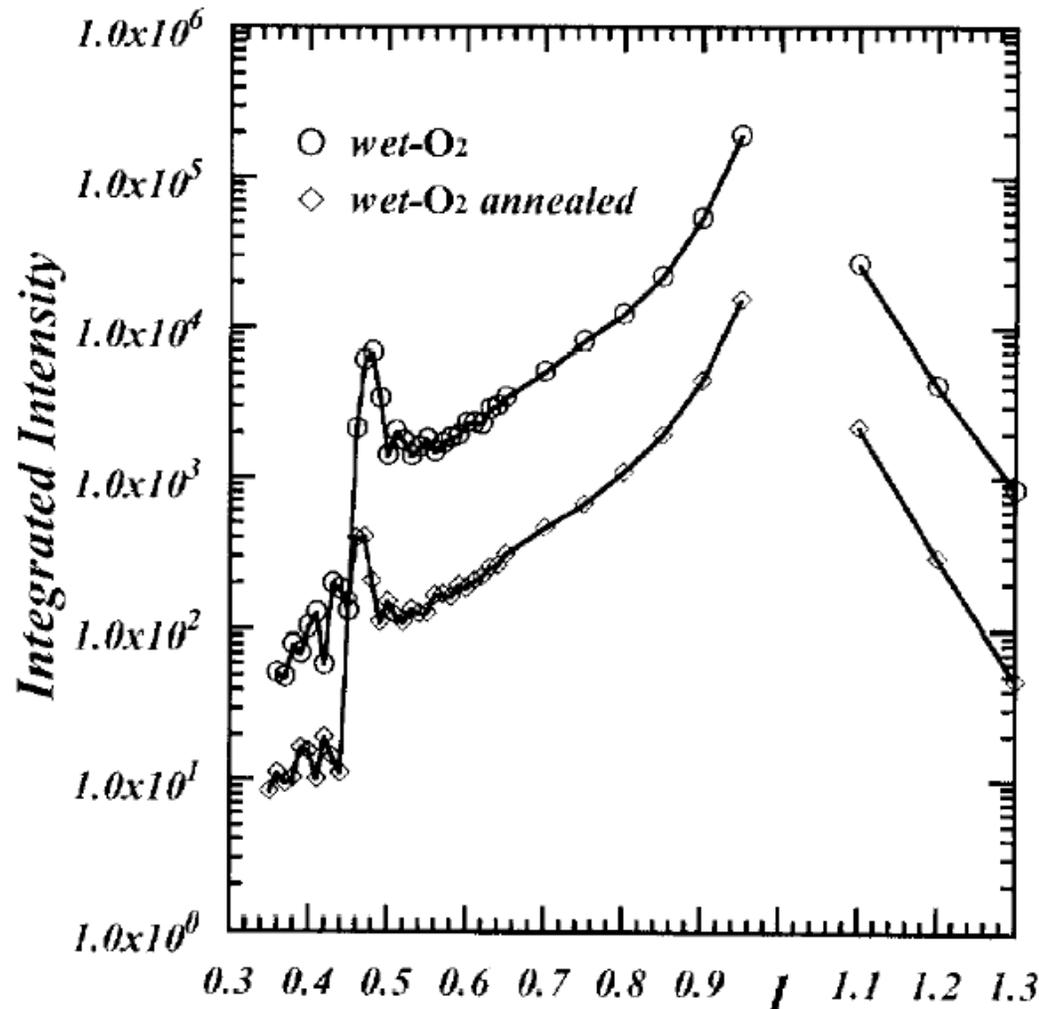
Can limit penetration to  $\sim 100\text{\AA}$



# Grown Oxide on Si(100)

I. Takahashi, K. Nakano, J. Harada, T. Shimura and M. Umeno, Surf Sci **315** L1021 (1994)

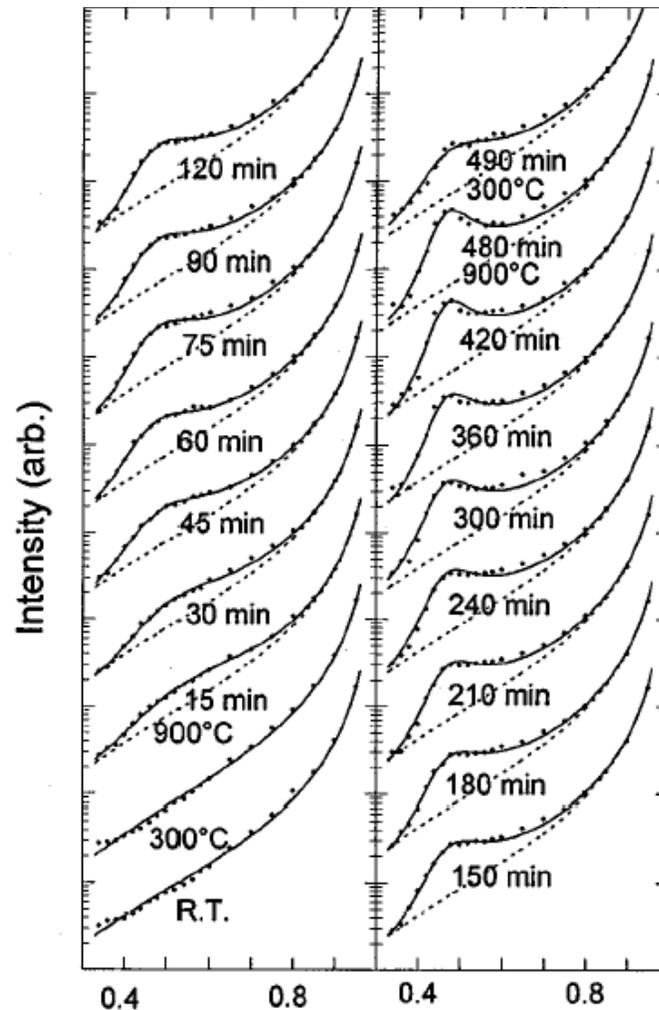
I. Takahashi, S. Okita, N. Awaji, Y. Sugita and S. Komiya, Physica B **245** 306 (1998)



I. K. Robinson, DOE Corrosion Contractors, Brookhaven, September 2002

# Growth of Thermal Oxide on Si(100)

N. Awaji, Y. Sugita, Y. Horii, and I. Takahashi, Appl. Phys. Lett. 74 2669 (1999)

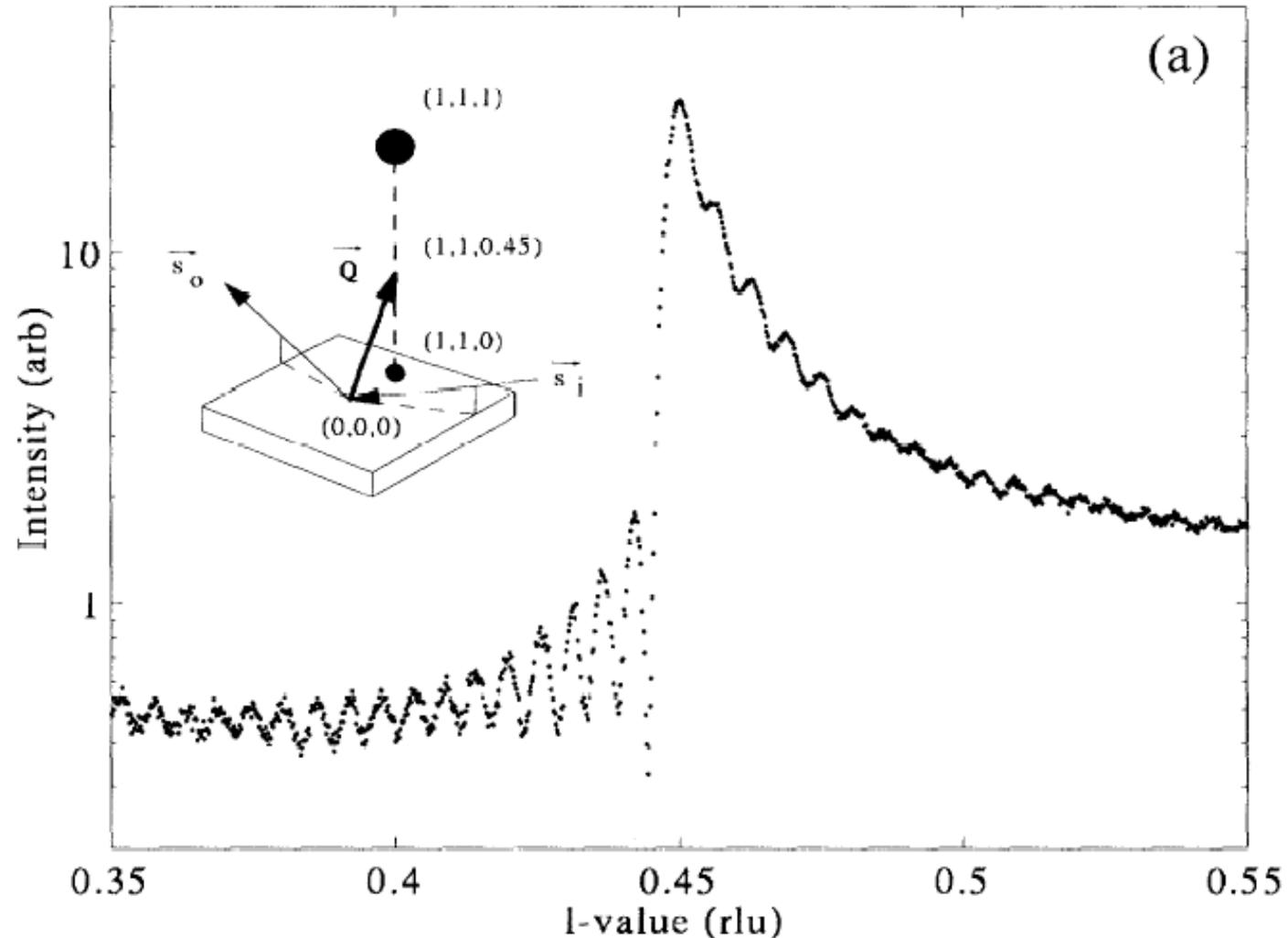


Atmospheric pressure  
O<sub>2</sub>:N<sub>2</sub> ratio 1:9  
(1,1,L) CTR

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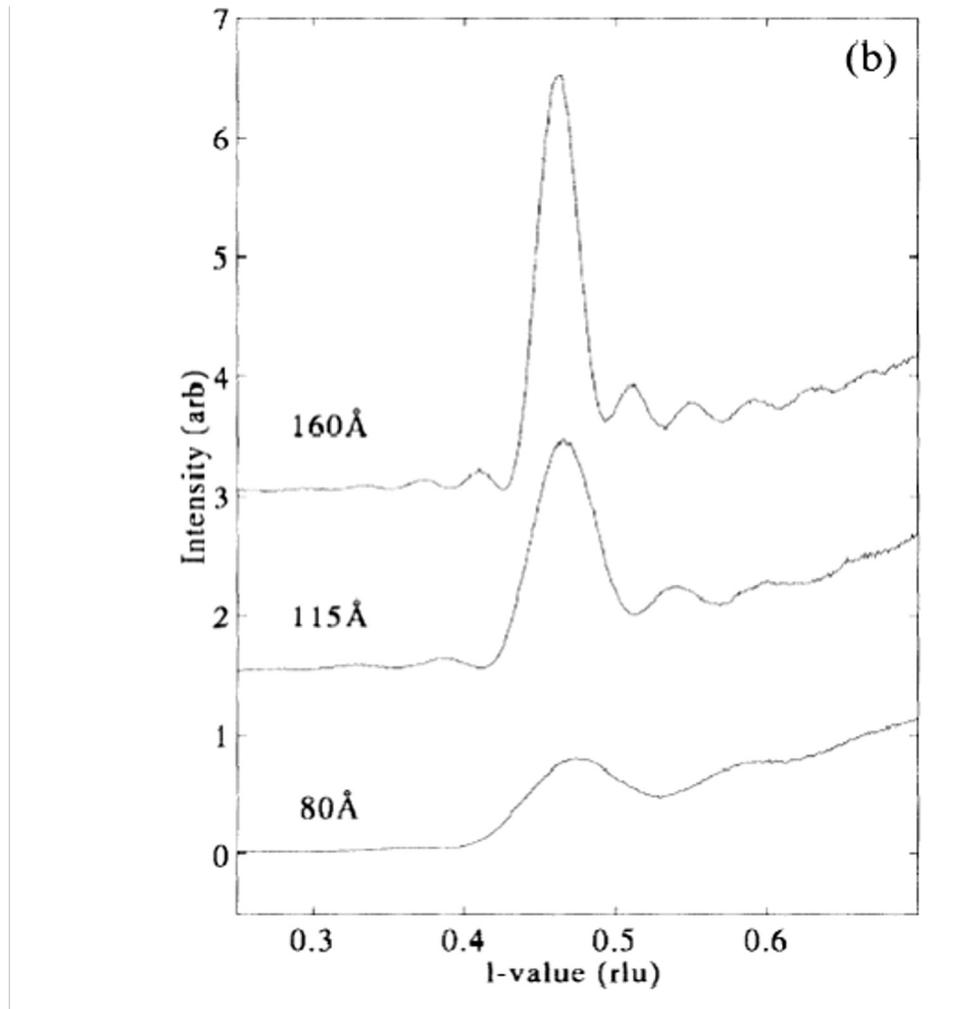
# 1000Å Oxide on Si(100) “Steam Process”

A. Munkholm, S. Brennan, F. Comin and L. Ortega, Phys. Rev. Lett. **75** 4254 (1995)



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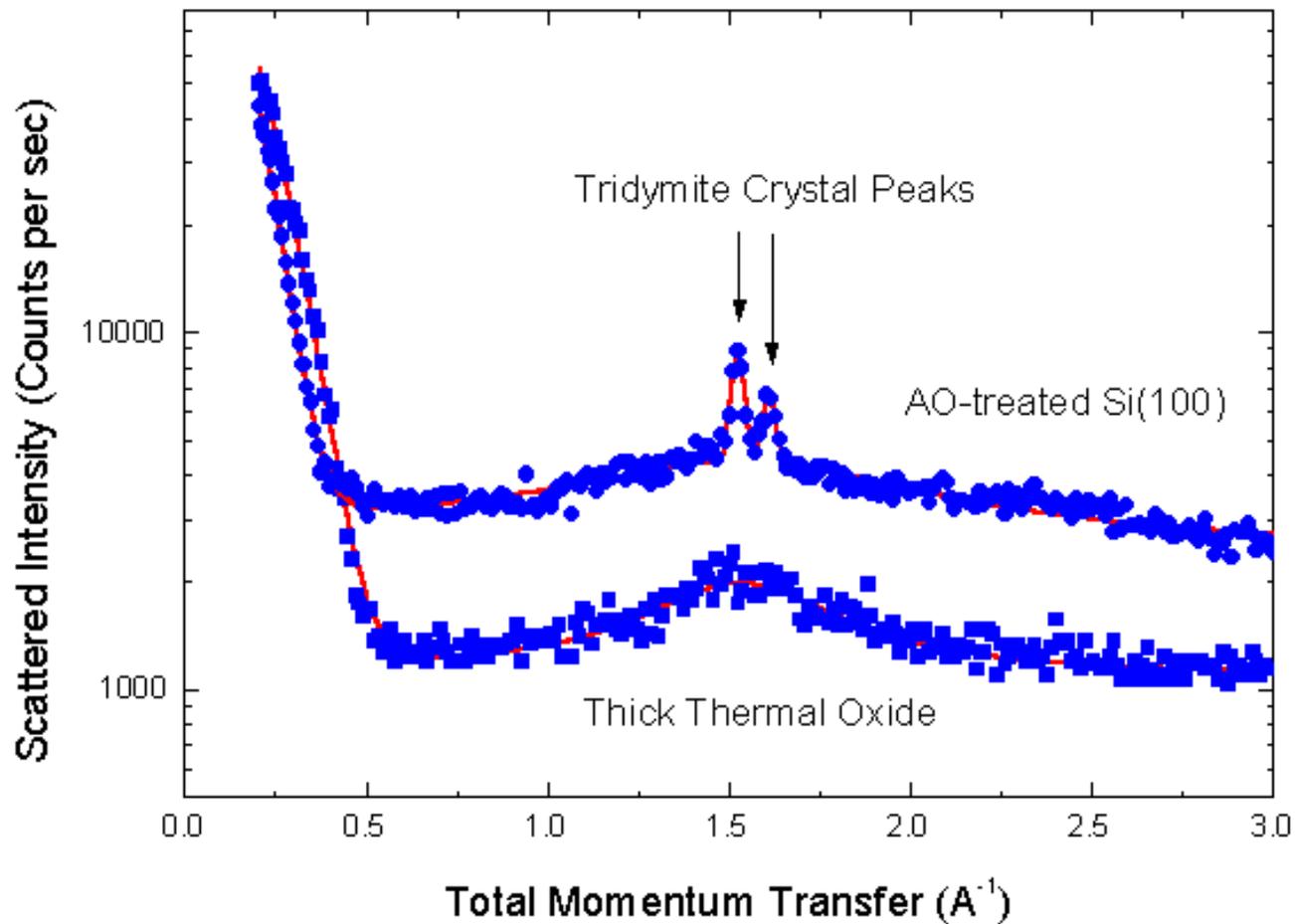
# Peaks scale with Thickness



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# Grazing Incidence Diffuse Scattering

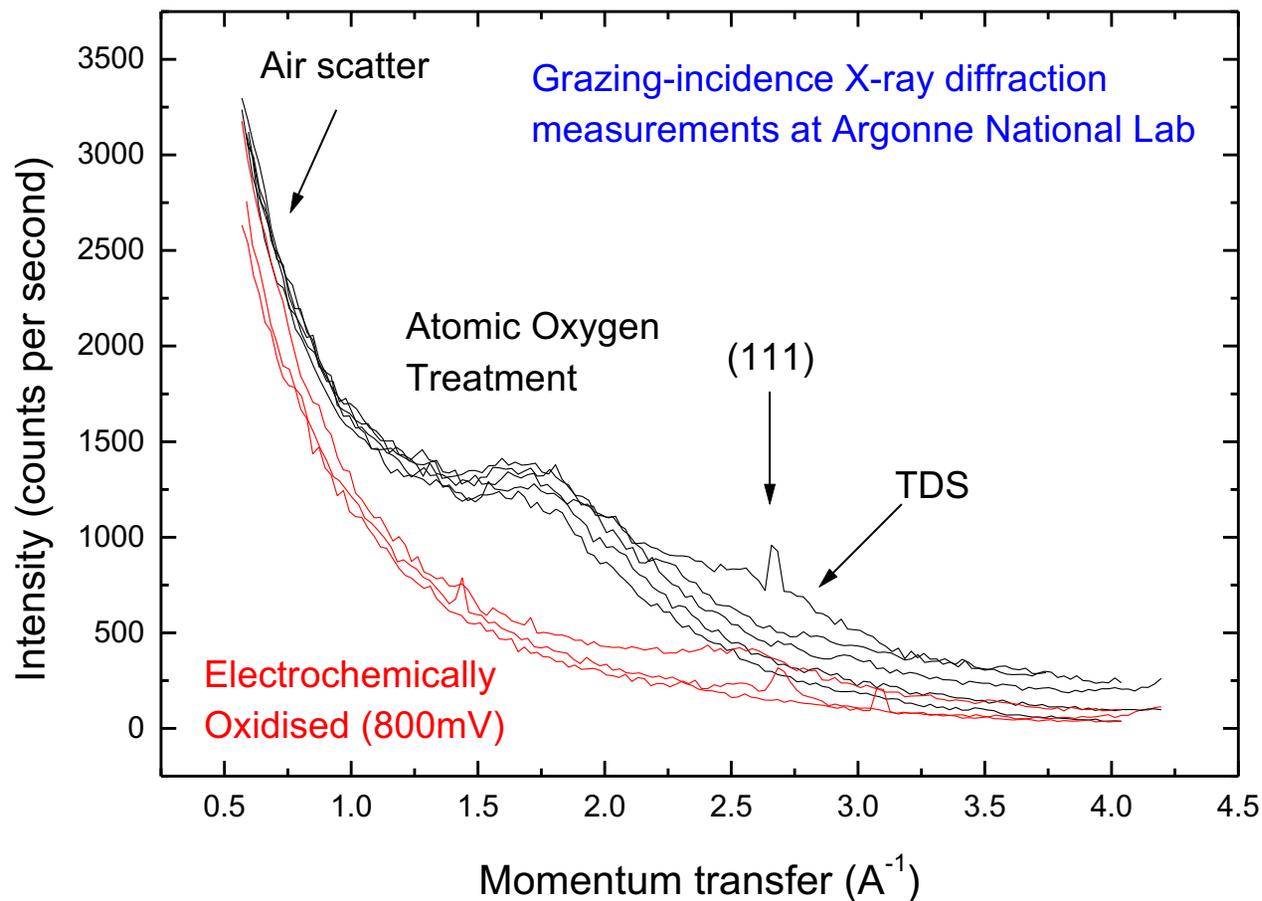
Atomic O oxidation by Tim Minton (Montana)



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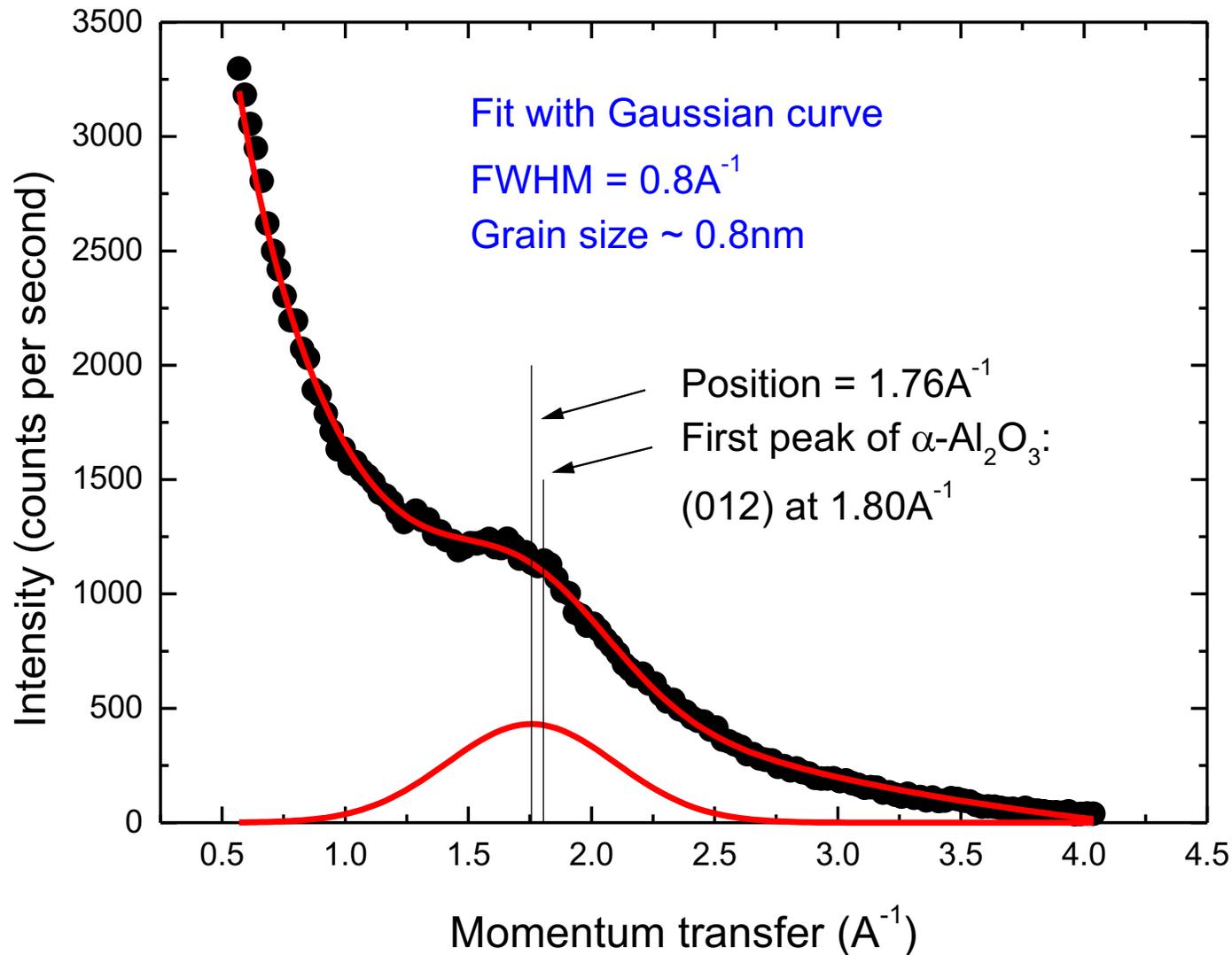
# Oxidation of Al(111) Single Crystals

Atomic O oxidation by Tim Minton (Montana)  
Electrochemical oxidation by Paul Natishan (NRL)



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# Aluminum Oxide Structural Properties

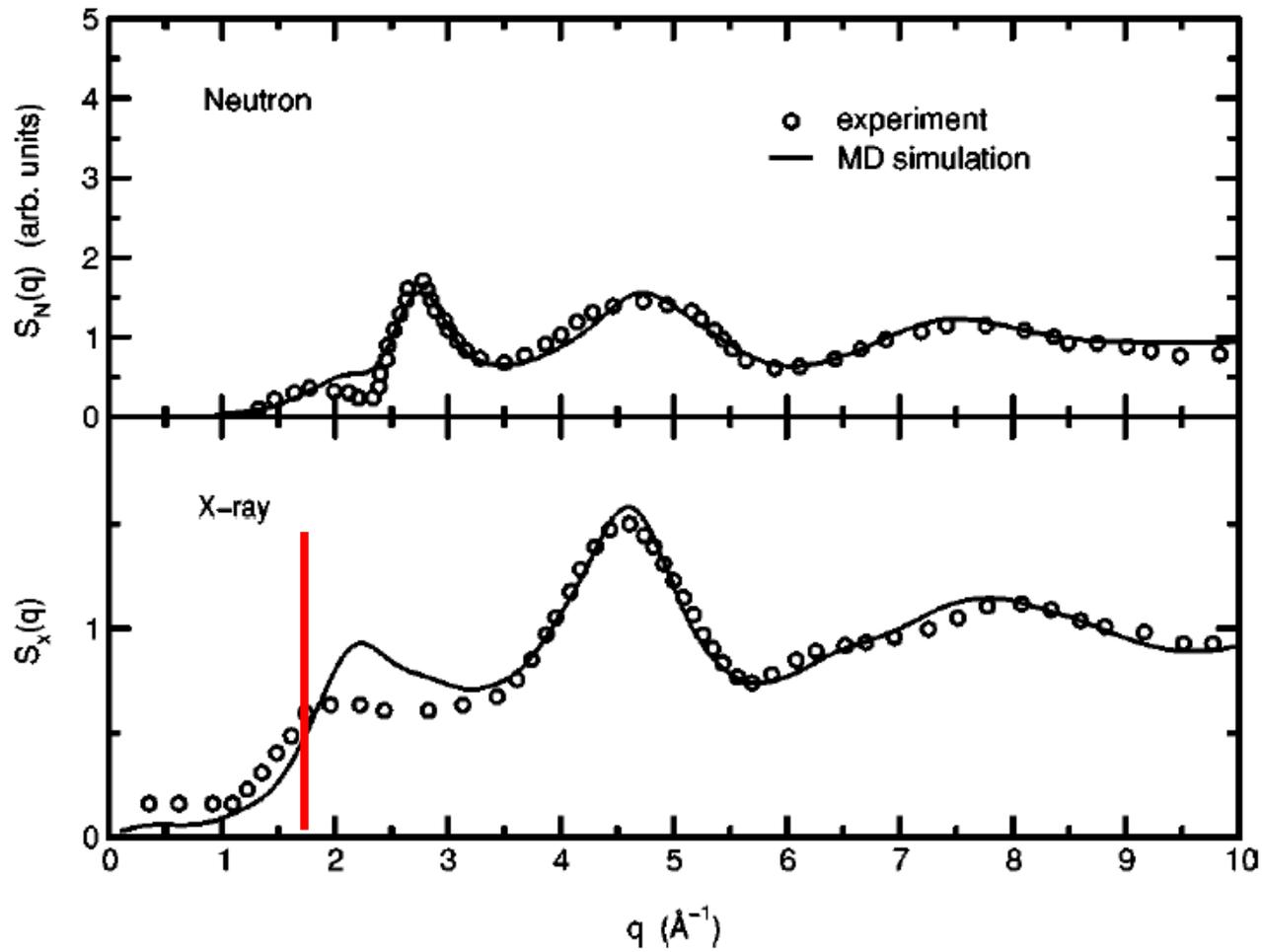


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# Structure Factor of Anodic $\text{Al}_2\text{O}_3$

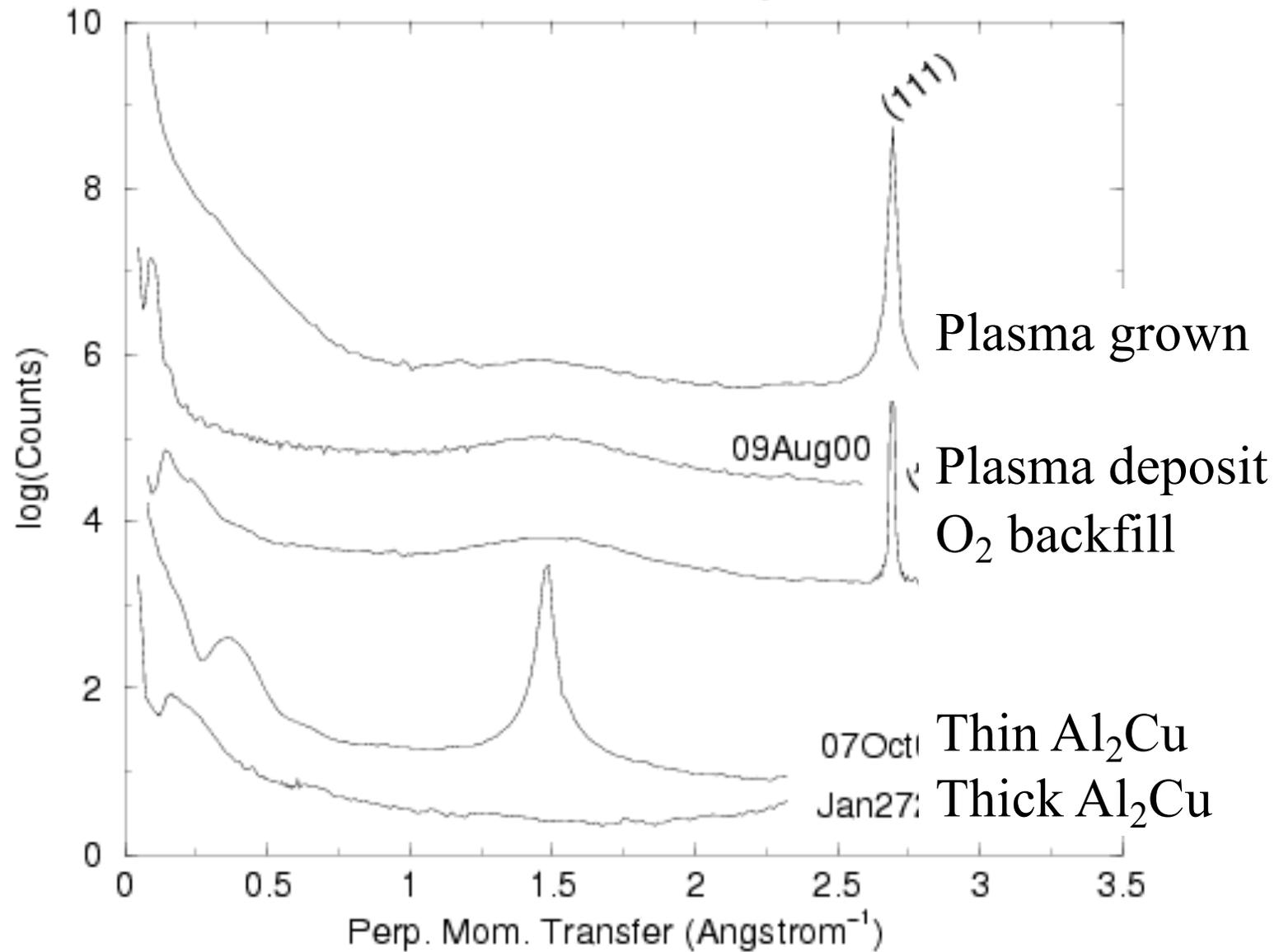
G. Gutierrez and B. Johansson, Phys. Rev. B. **65** 104202 (2002)

P. Lamparter and R. Kniep, Physica B **234** 405 (1997)



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# X-ray reflectivity of e-beam evaporated films on SiO<sub>2</sub>

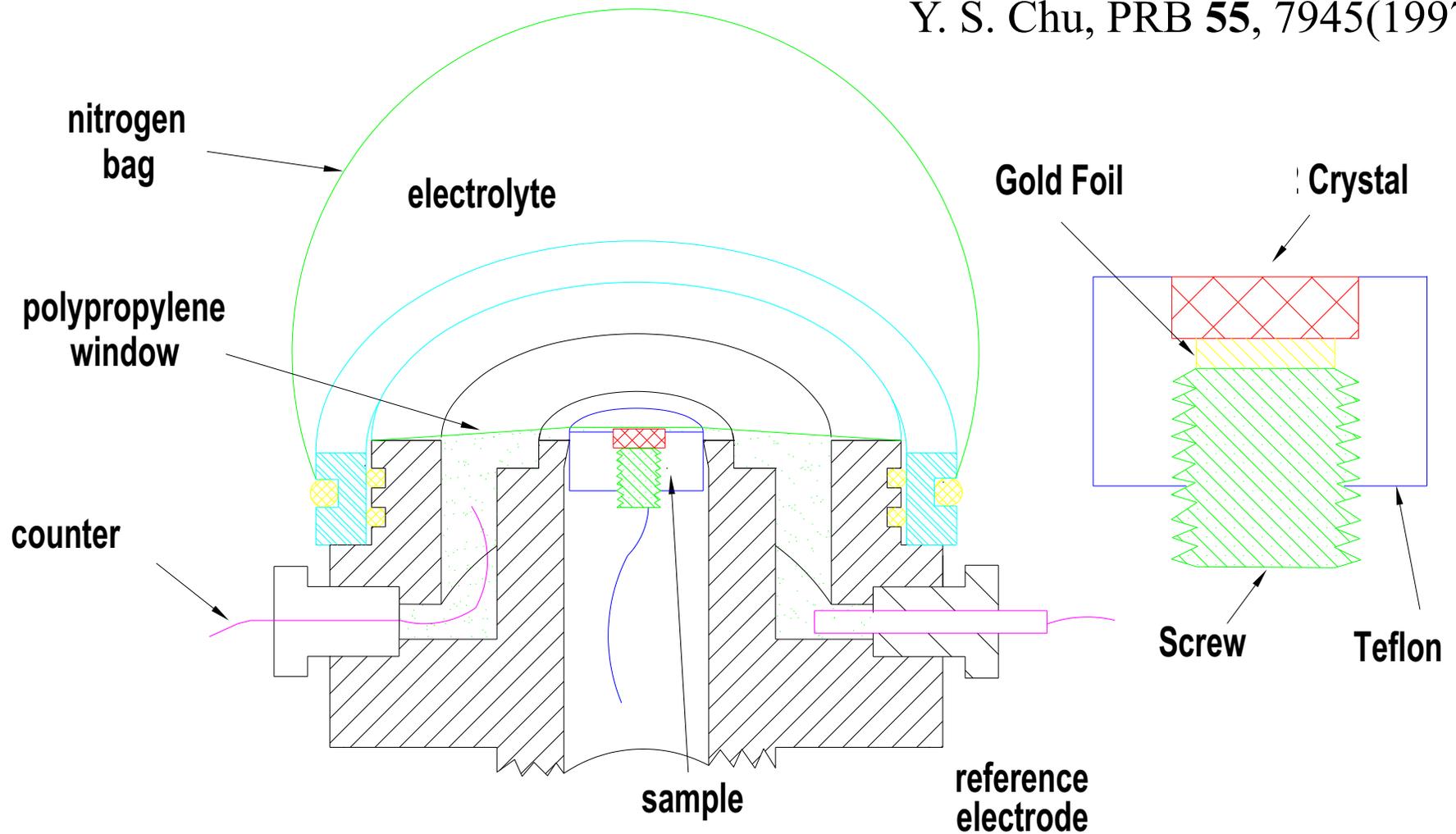


# Crystalline Oxides

- Structure of Cu(111)/H<sub>2</sub>O Interface
- Changes with Applied Potential
- Epitaxial Cu<sub>2</sub>O Oxide
- Thin Oxide is Defective

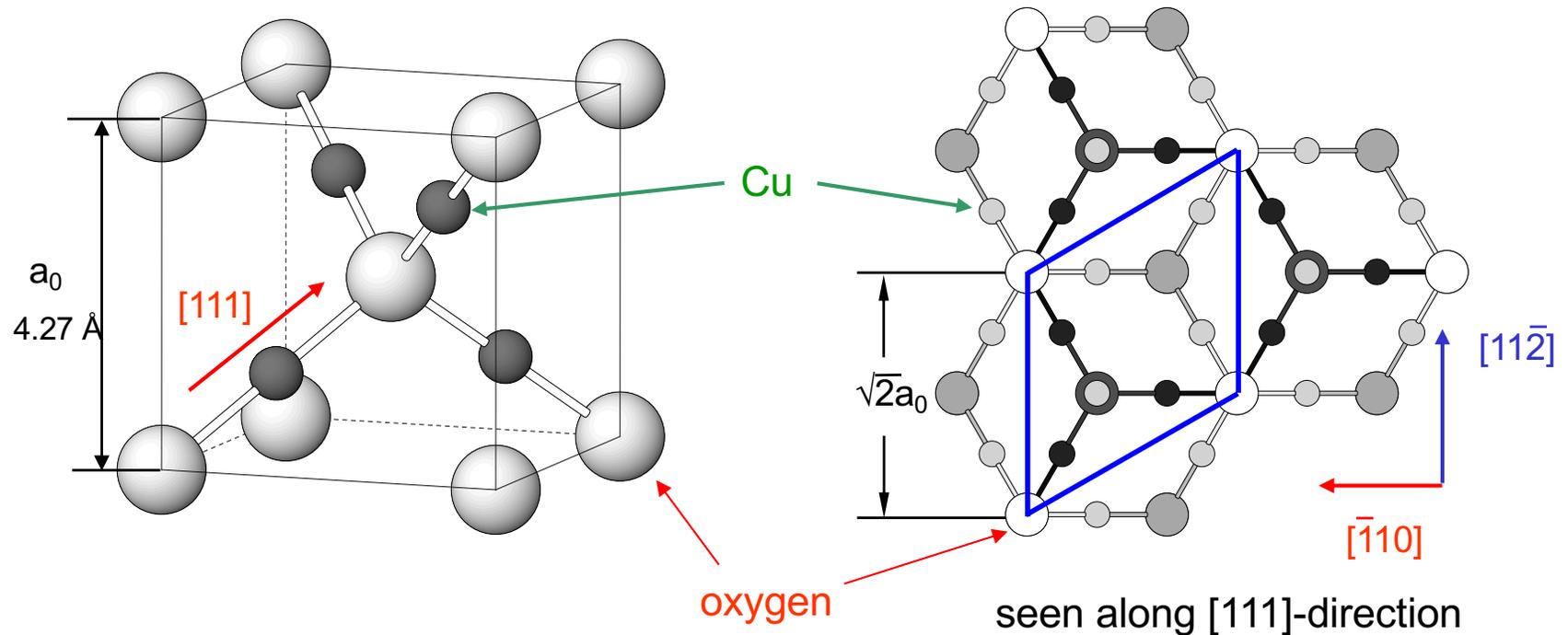
# Thin-layer *in-situ* Cell

Y. S. Chu, PRB **55**, 7945(1997)



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# Structure of Cuprite, $\text{Cu}_2\text{O}$



- 2 oxygen atoms + 4 Cu atoms in a bulk unit cell
- linear O-Cu-O bonds

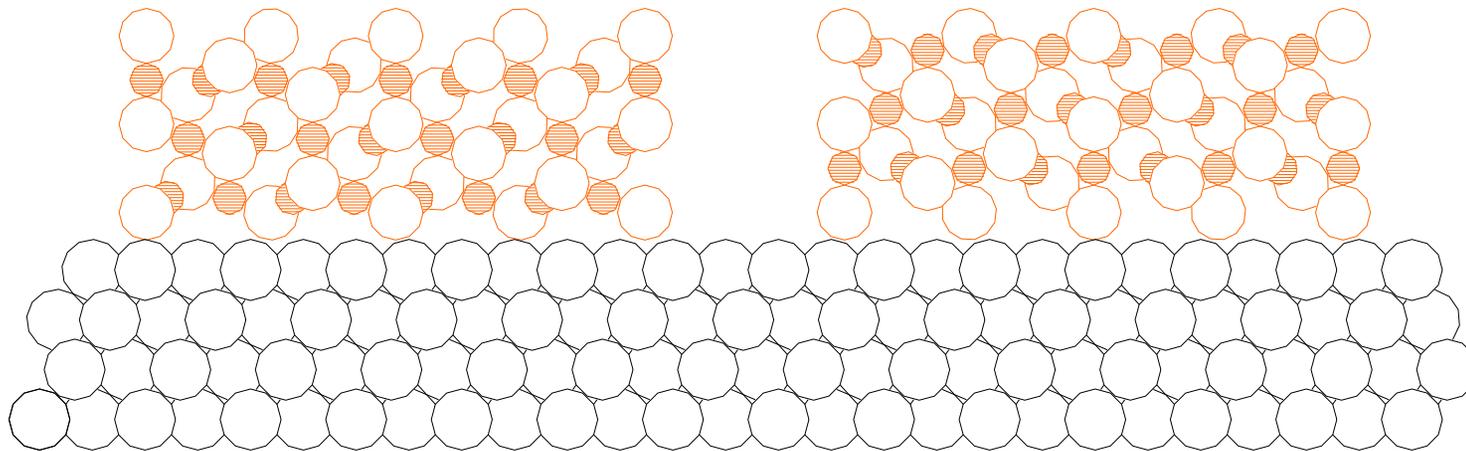
hexagonal surface unit cell

$$a = \sqrt{2}a_0 \quad c = \sqrt{3}a_0$$

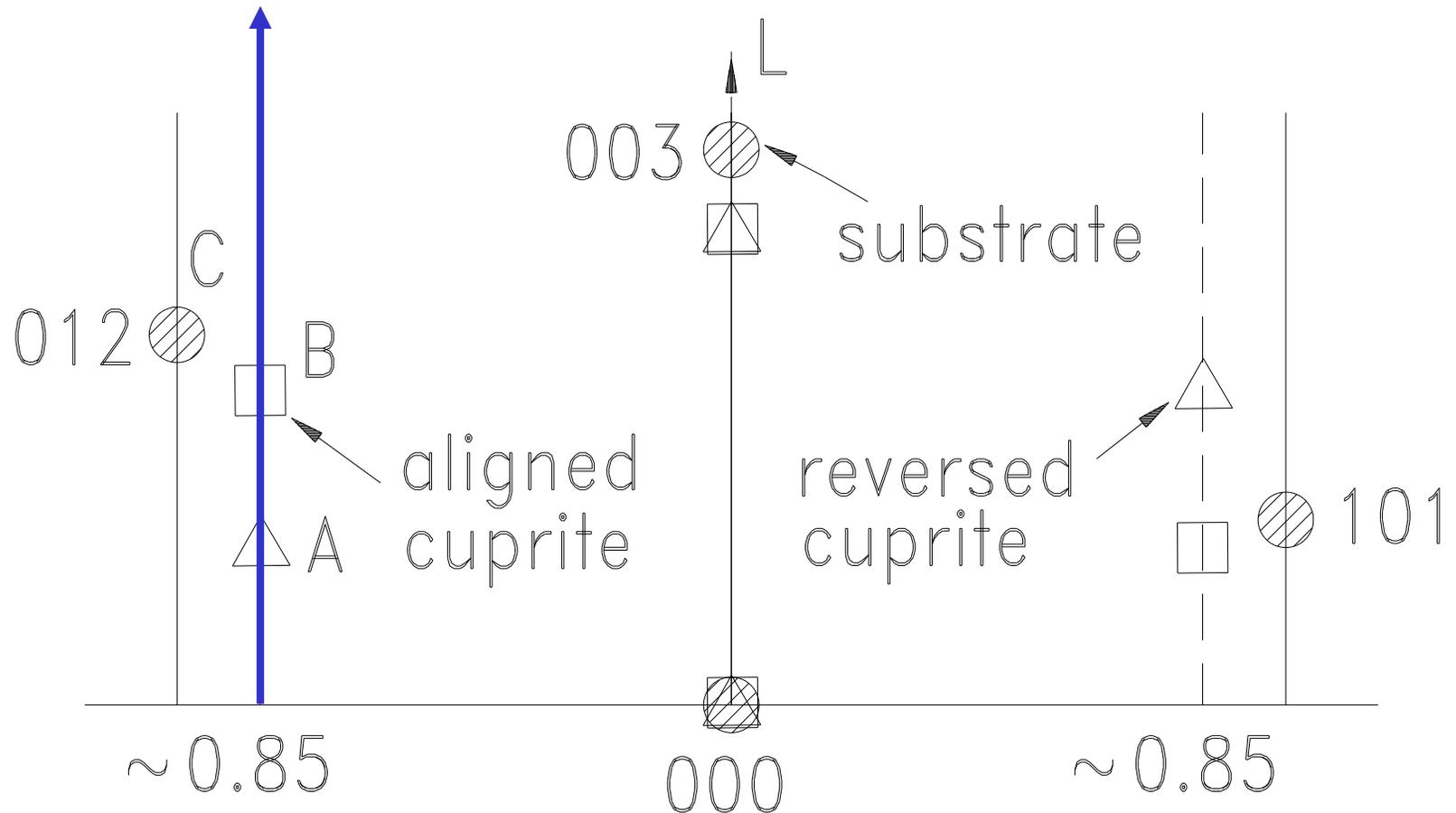
# Two Epitaxial Orientations

Reversed  
Oxide

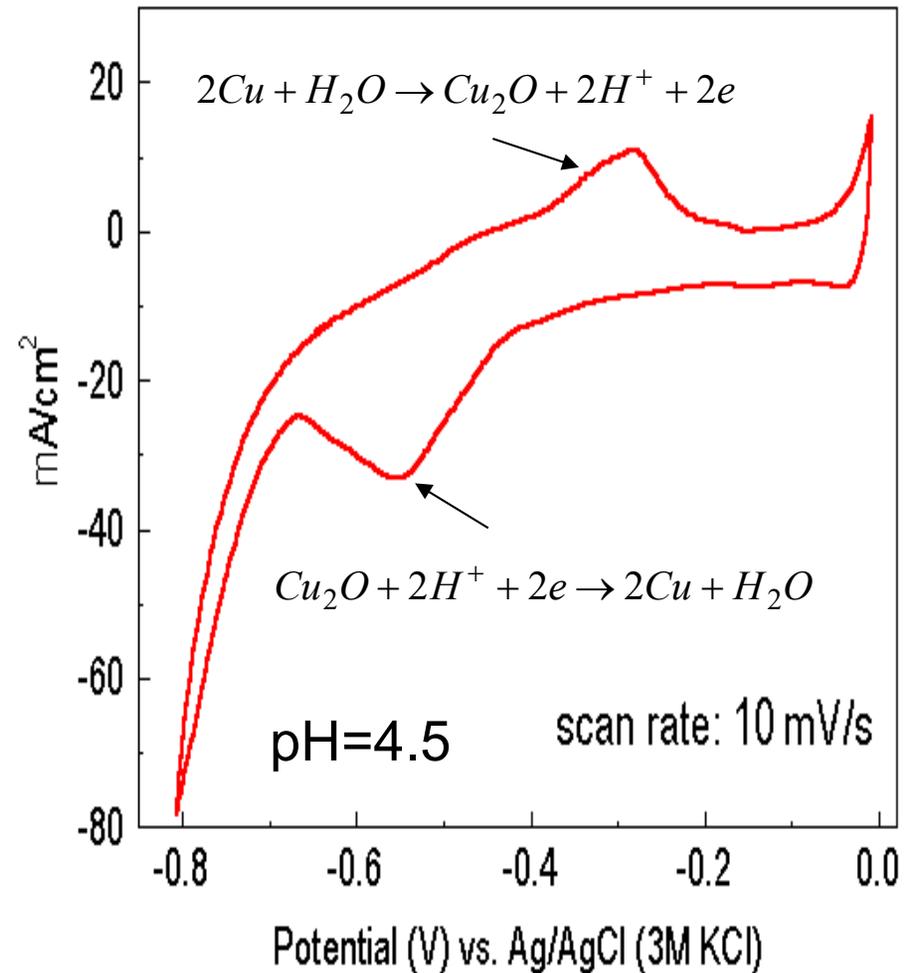
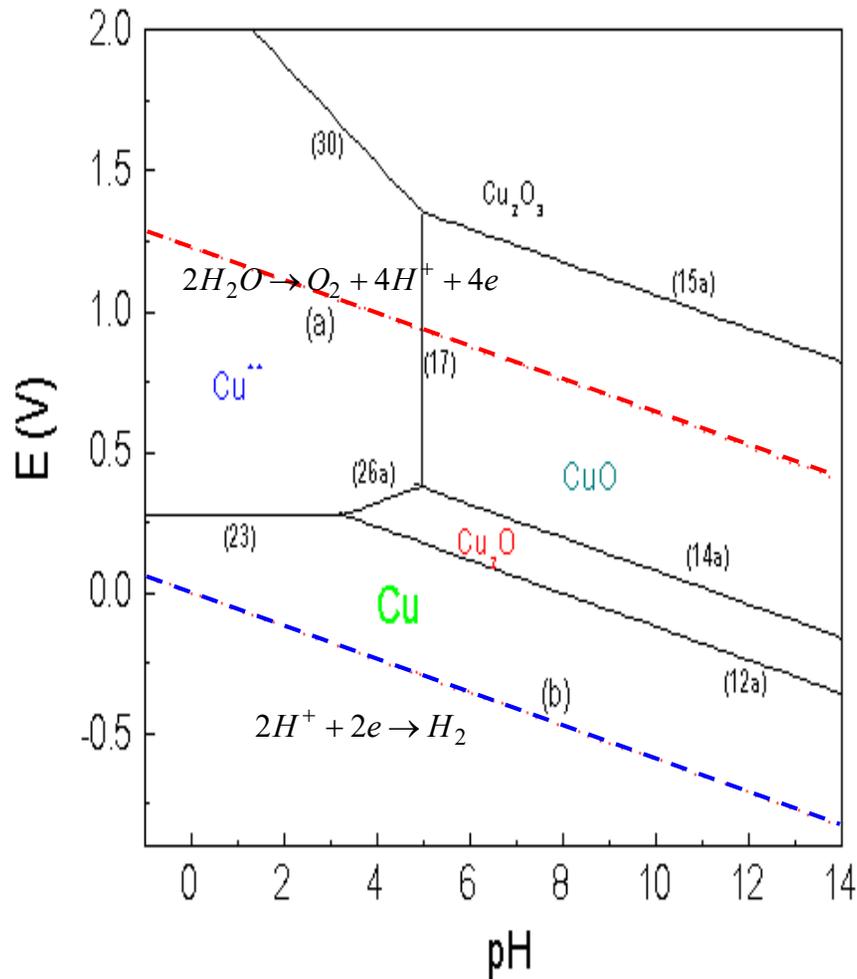
Aligned  
Oxide



# Hexagonal Coordinate System



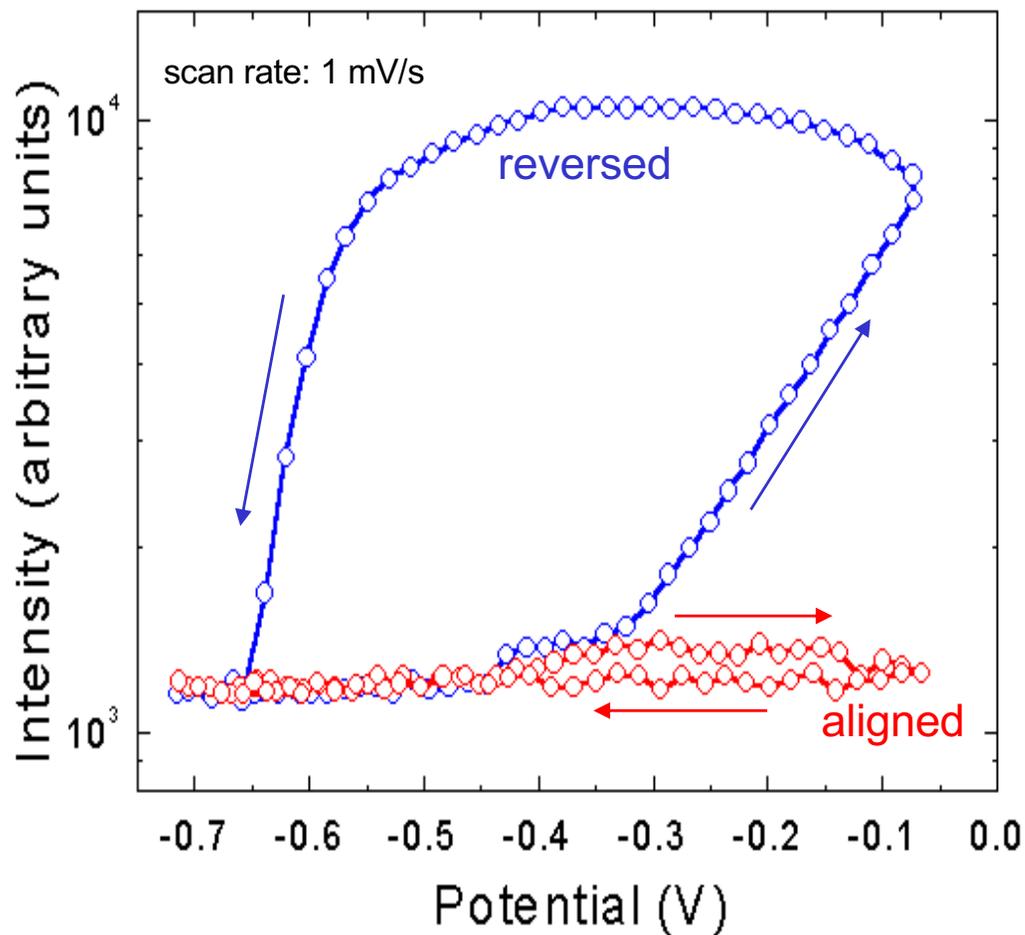
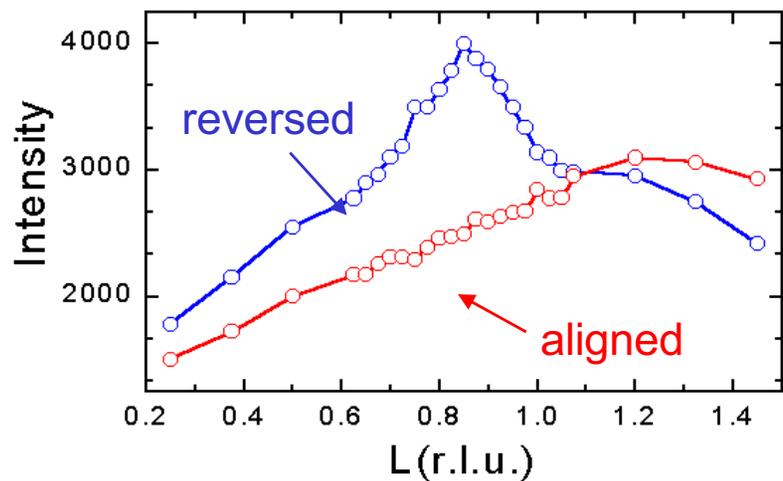
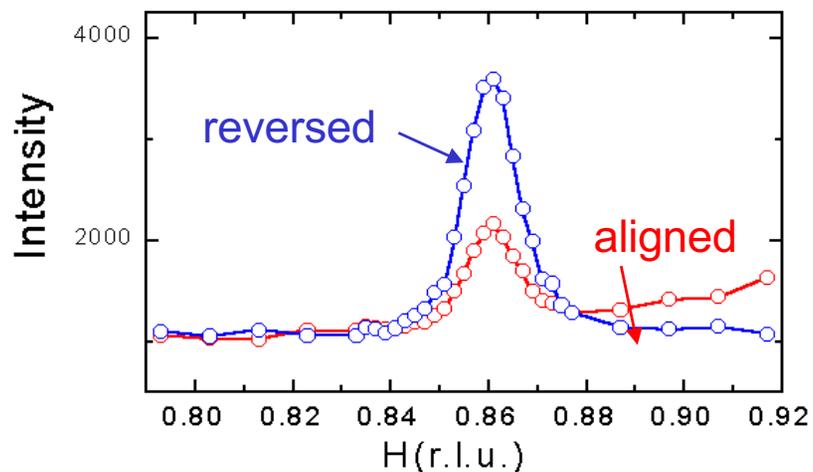
# Thermodynamic Equilibrium Cu/H<sub>2</sub>O



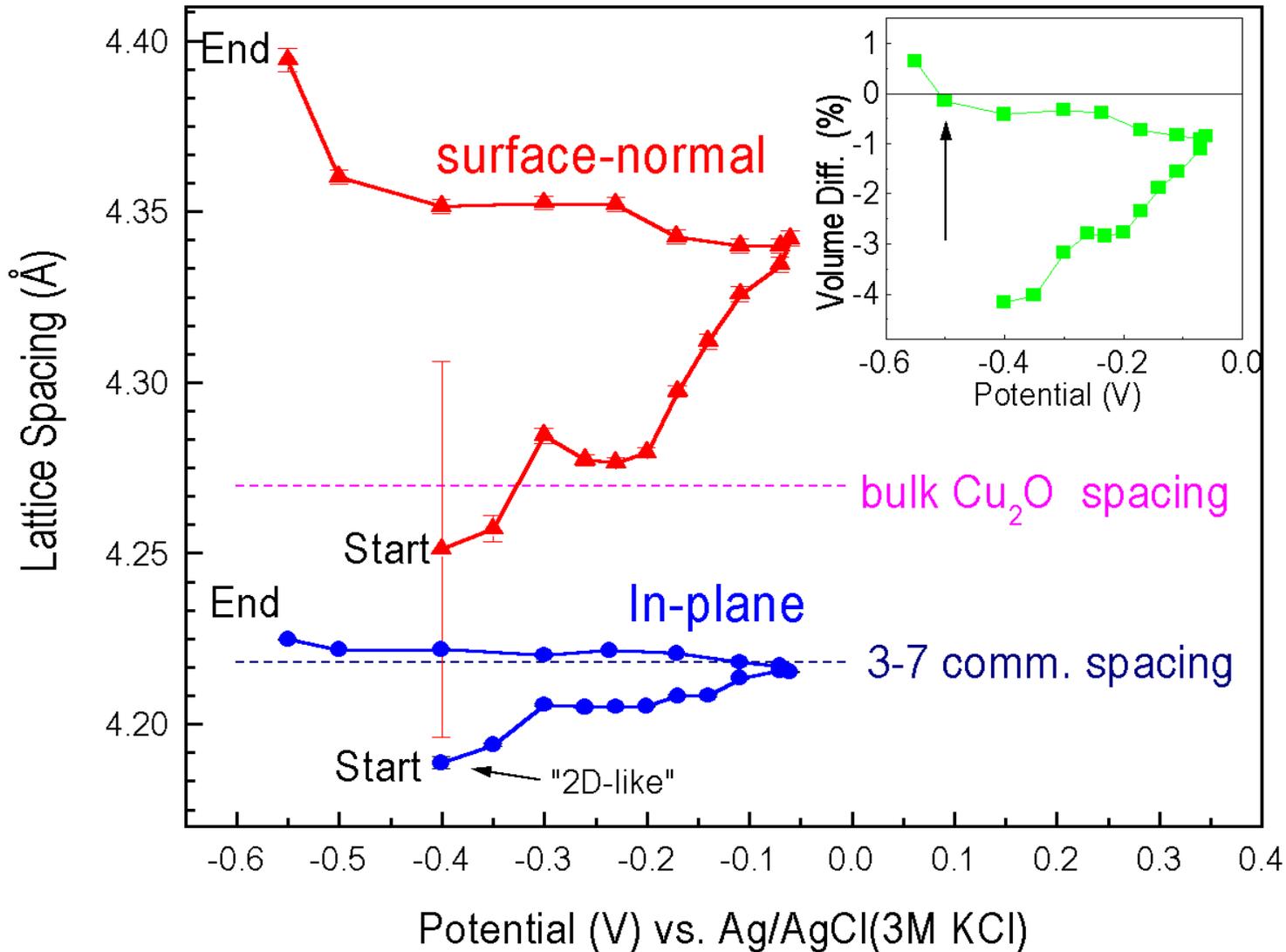
M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solution* (Pergamon, New York, 1966)

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# Thickening of Aqueous Oxides

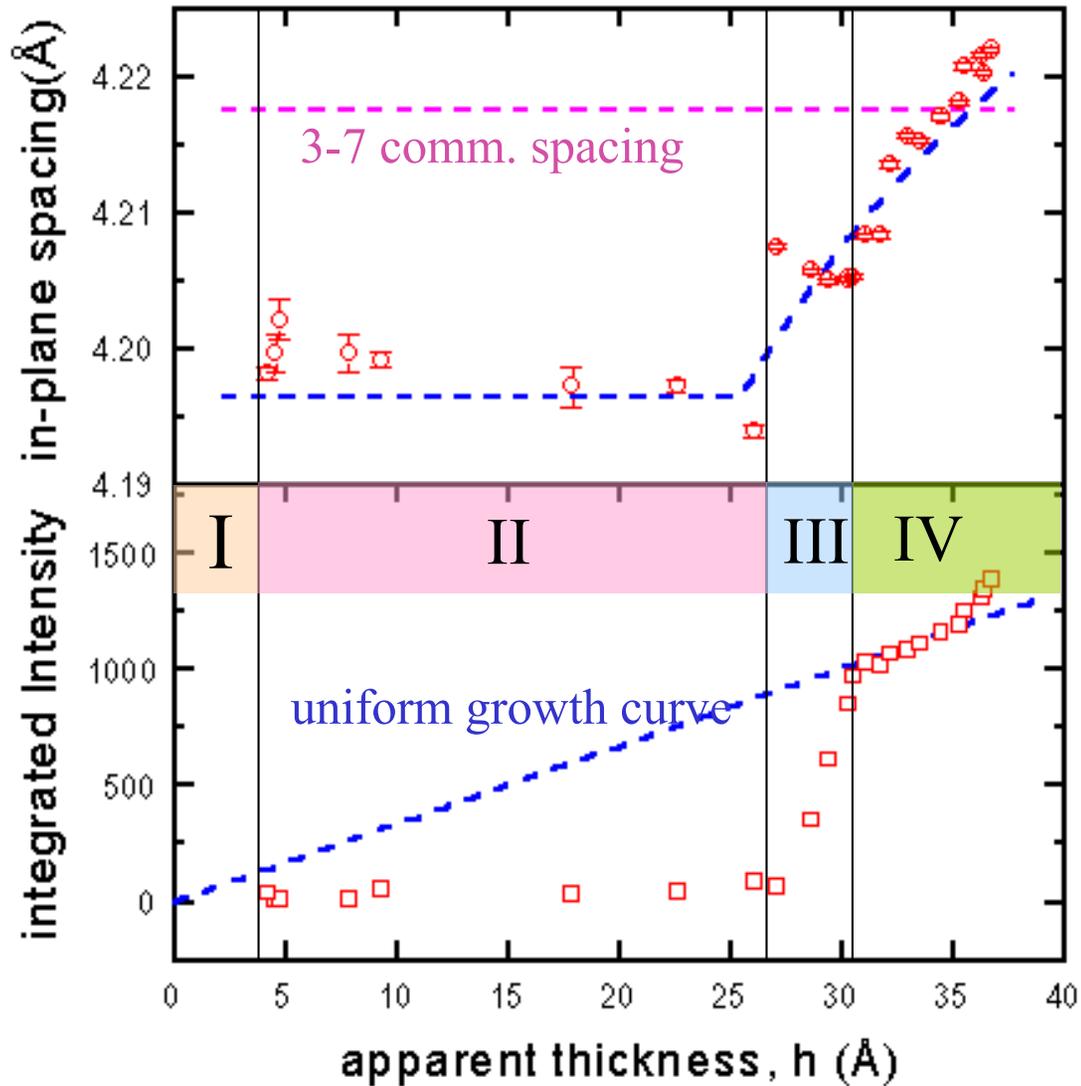


# Strain Evolution During Oxidation



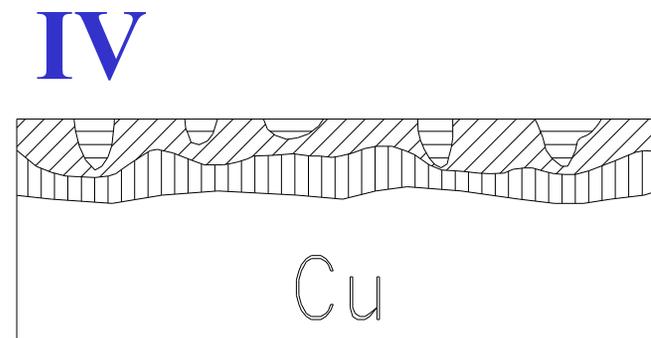
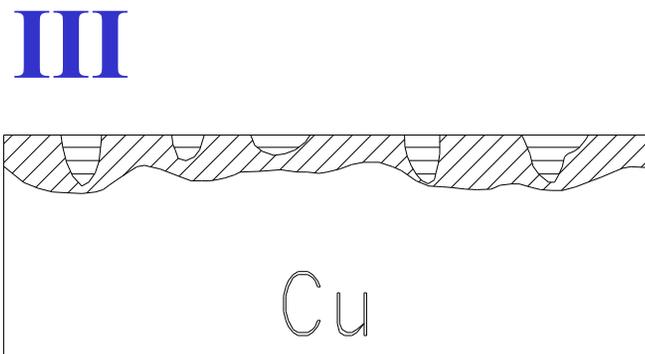
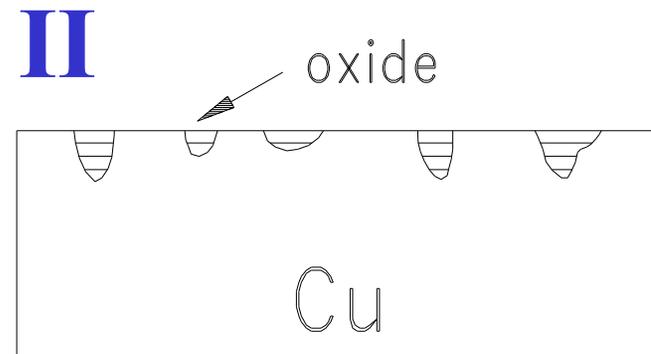
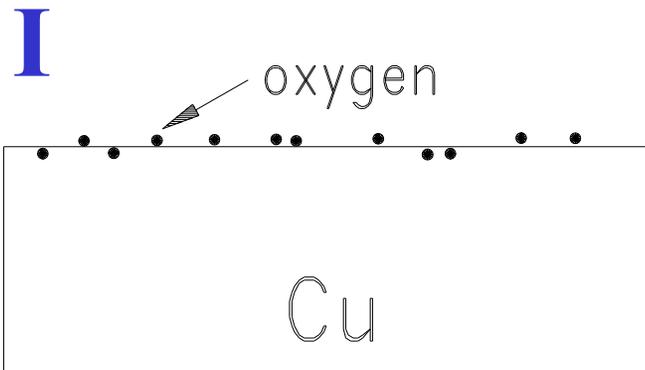
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# Four Stages of Growth

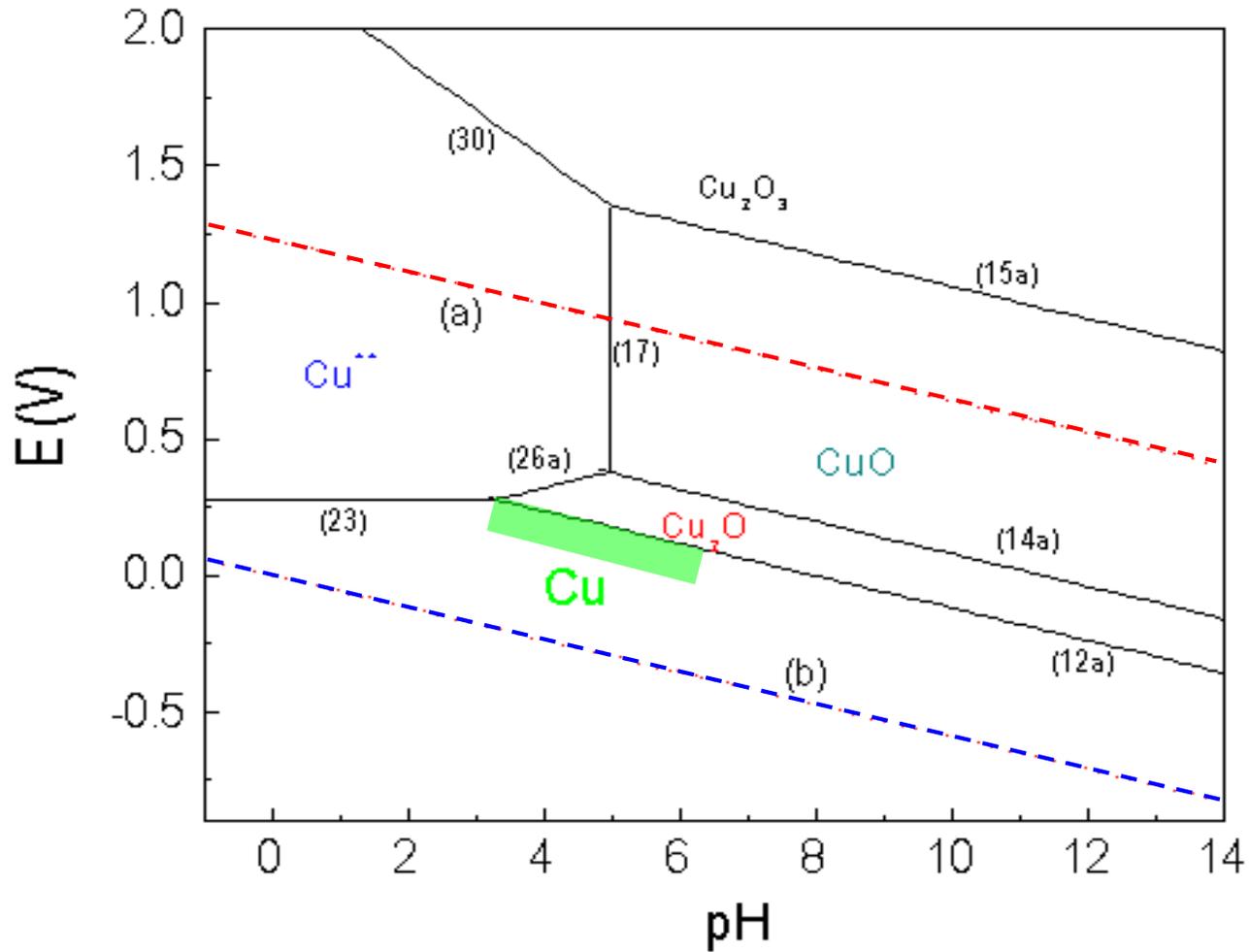


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# Pictures of Growth Stages



# Surface Phase in Pourbaix Diagram



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# Conclusions

- Diffraction Methods are more Effective for Crystalline Oxides
- Thin  $\text{Cu}_2\text{O}$  Oxide Films are Defective
- Grazing Incidence needed for Amorphous Oxide Films
- Possibility to see Differences in Short-Range Order in Amorphous Oxides