Probing Copper Adsorbates at Silica Surfaces using Integrated Planar Optical Waveguides

(Subtask C-3-3)

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Goal

Develop an *in-situ* probe to selectively detect both Cu^{2+} and Cu^{o} at the silica - solution interfaces

Purpose: monitor the desorption and adsorption process of copper species in semiconductor surfaces during rinse stages

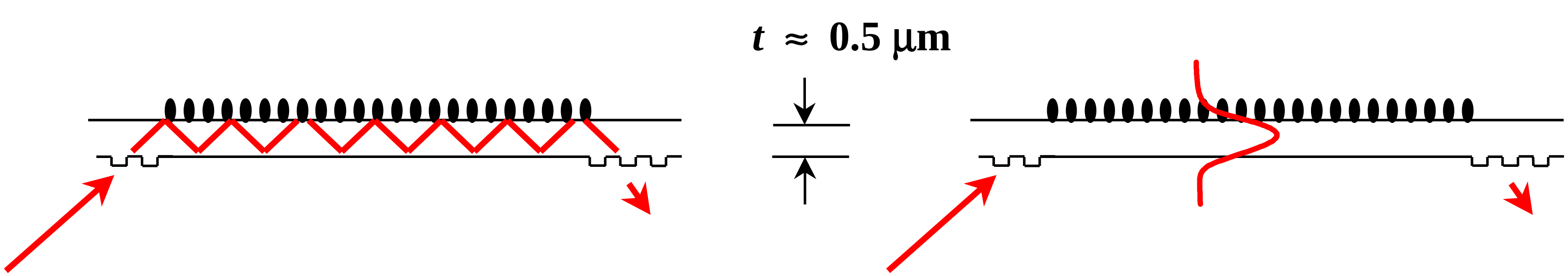
Employed Technique

Integrated Optical Waveguide Absorption Spectrometry

How it works

Ray Optics model

Wave model



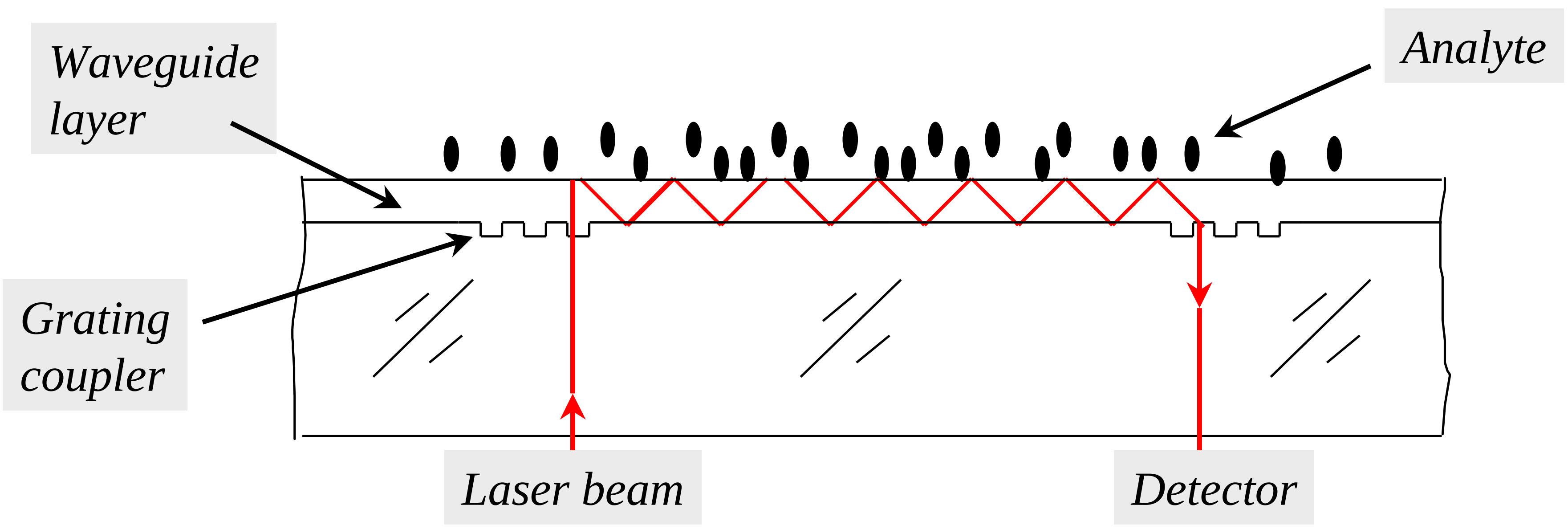
Advantages

- Surface selectivity: guided mode confinement
- Spectroscopic selectivity to probe specific species
- High sensitivity: long interaction length
- *In-situ* and real-time detection
- Cost effective: mass manufactured, ease of integration

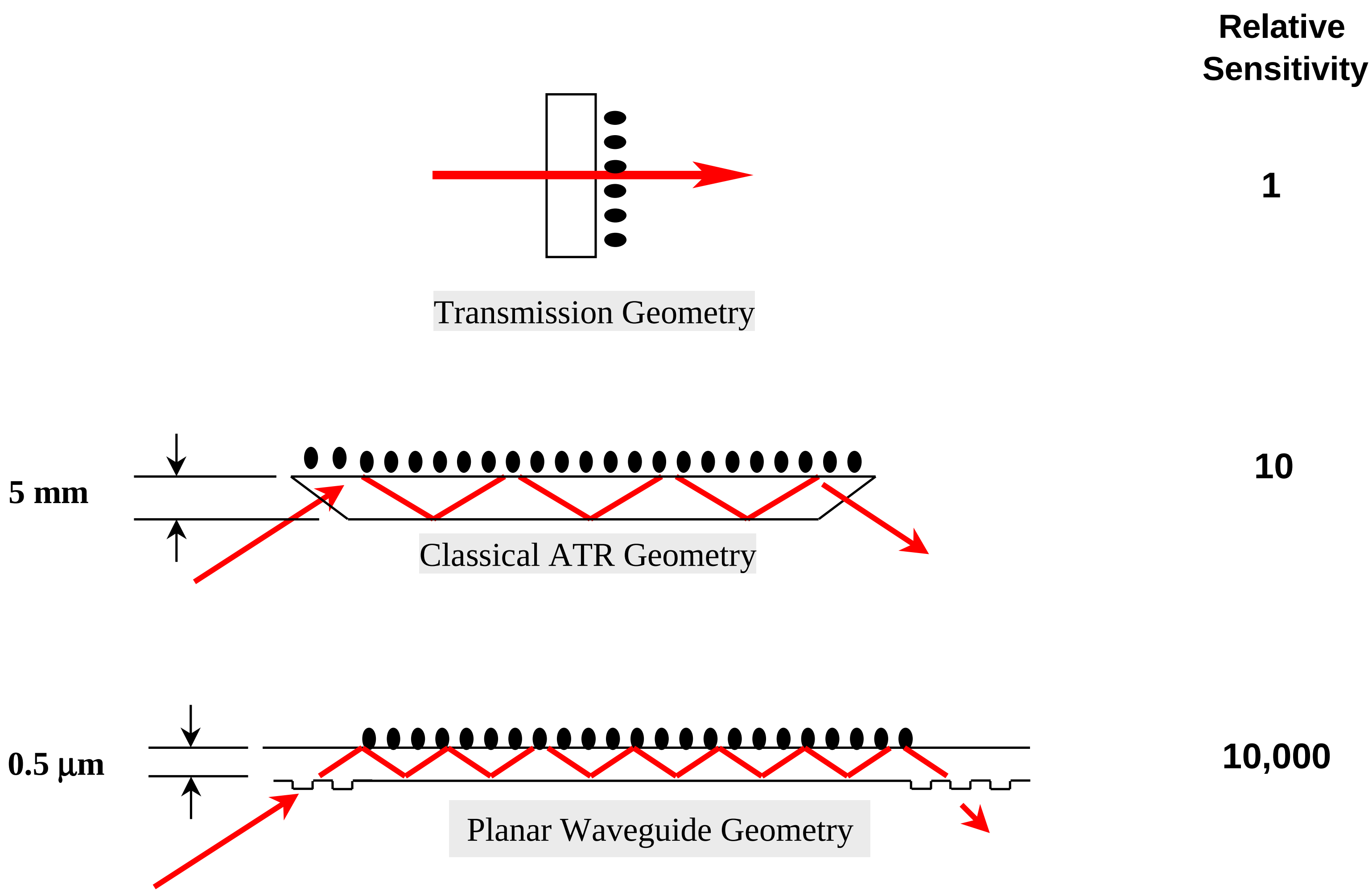
What is a Planar Optical Waveguide?

• A higher refractive index layer that confines a propagating light beam

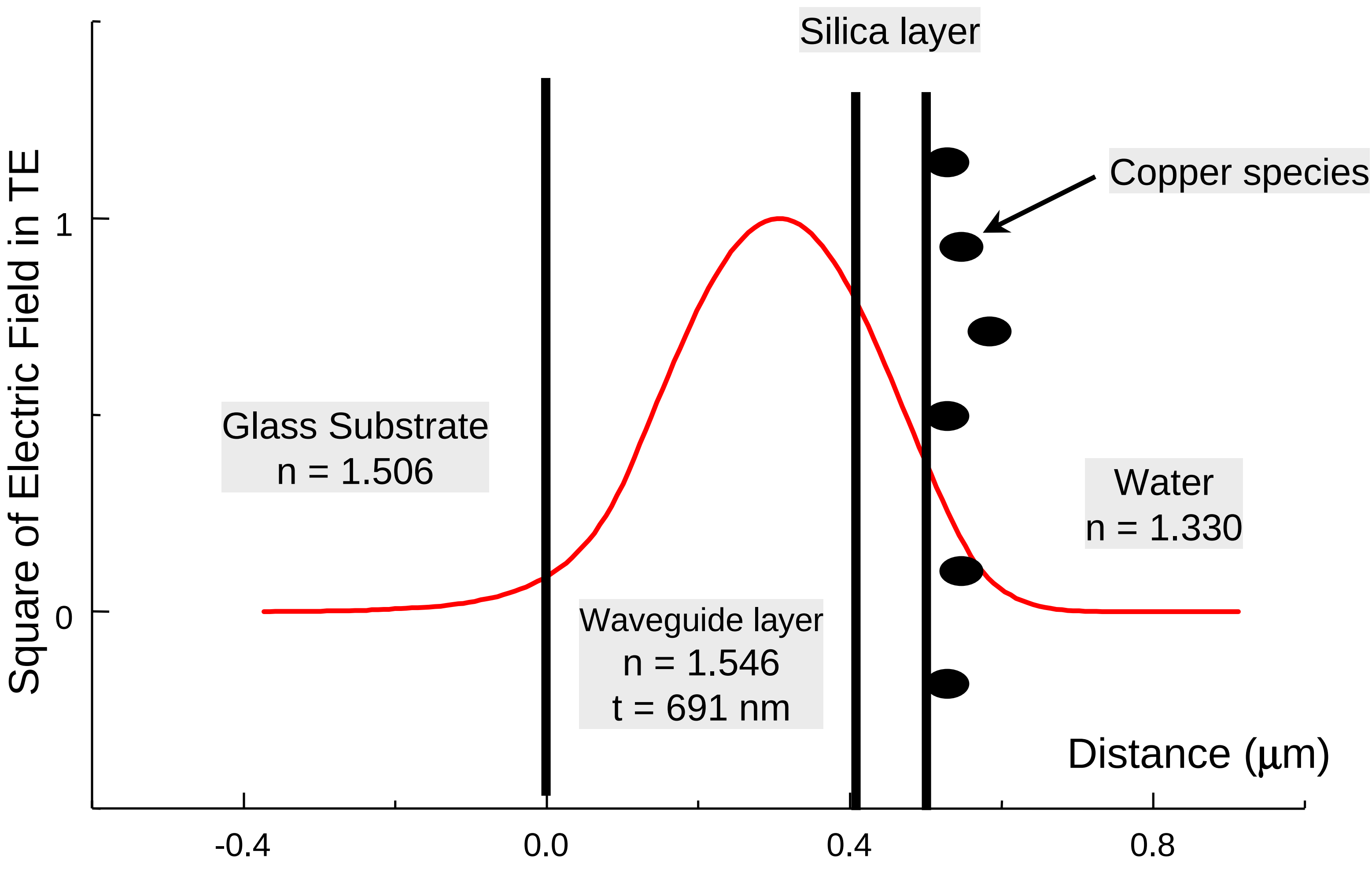
• Extremely high sensitivity for probing interfacial phenomena



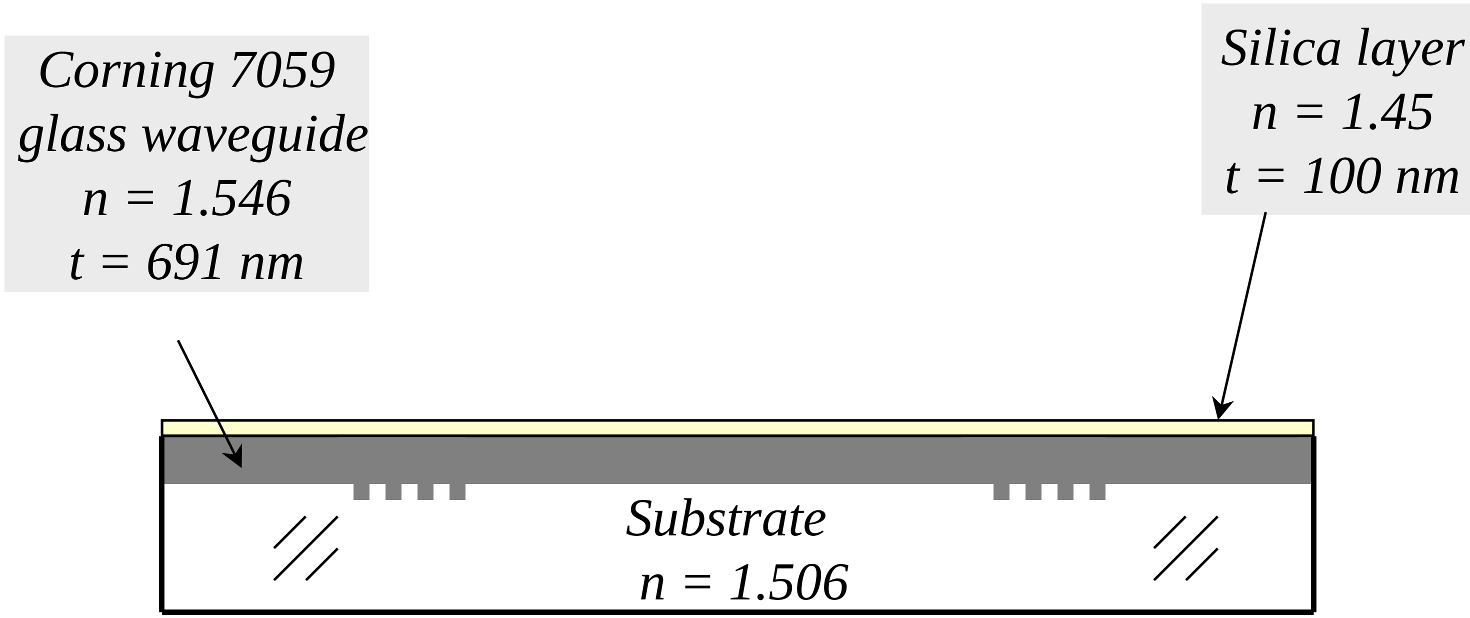
Spectroscopic Formats



Copper Detection



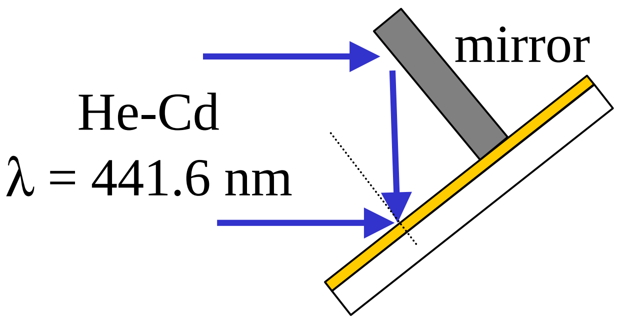
RF Sputtering deposited Waveguide Films



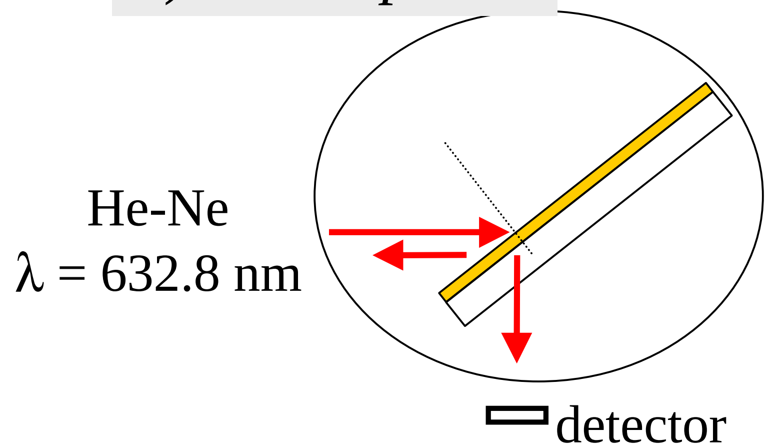
Propagation loss = 1 dB / cm

Surface Relief Grating Fab

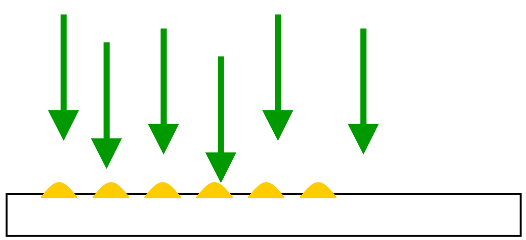
1) *Holographic Exposure*



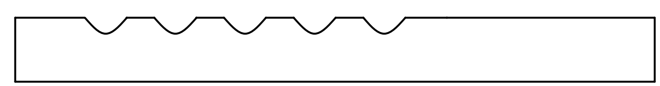
2) *Development*



3) *Argon Ion Milling*

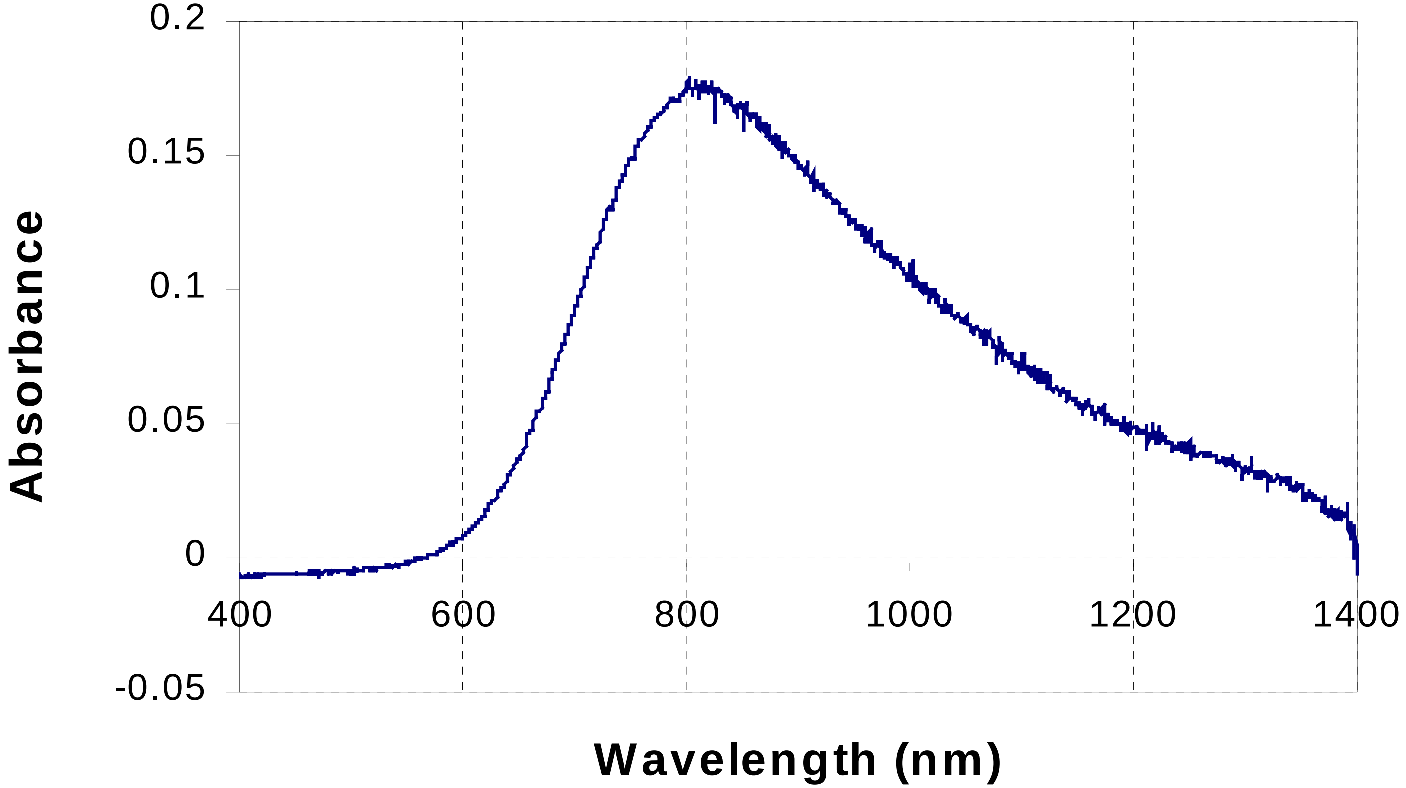


4) *Surface Relief Grating*

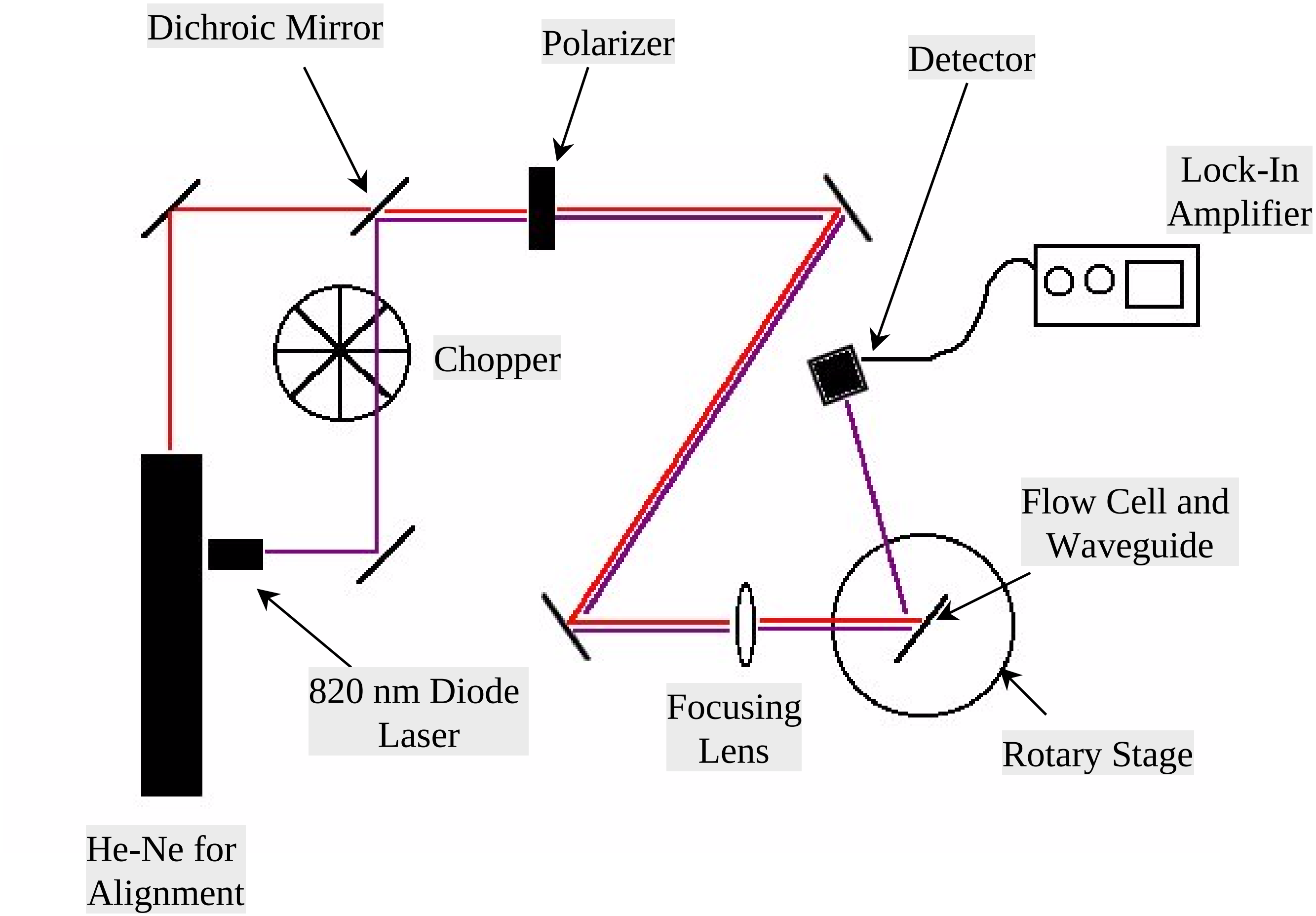


Choice of Analytical Wavelength: Spectra of Cu^{2+}

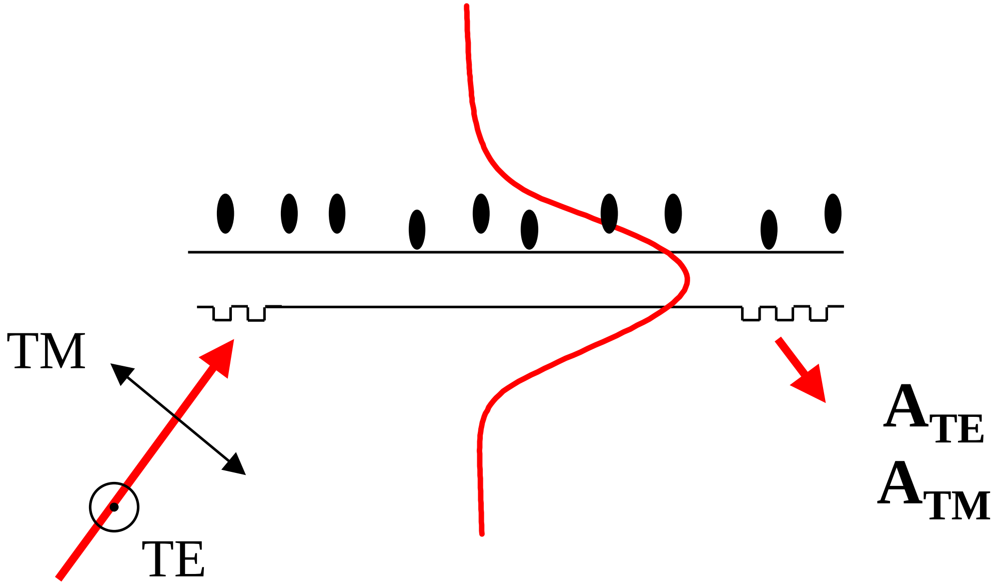
1,000 ppm



Experimental Setup for Copper Detection



Two Independent Measurements of the Surface Coverage with the Same Probe

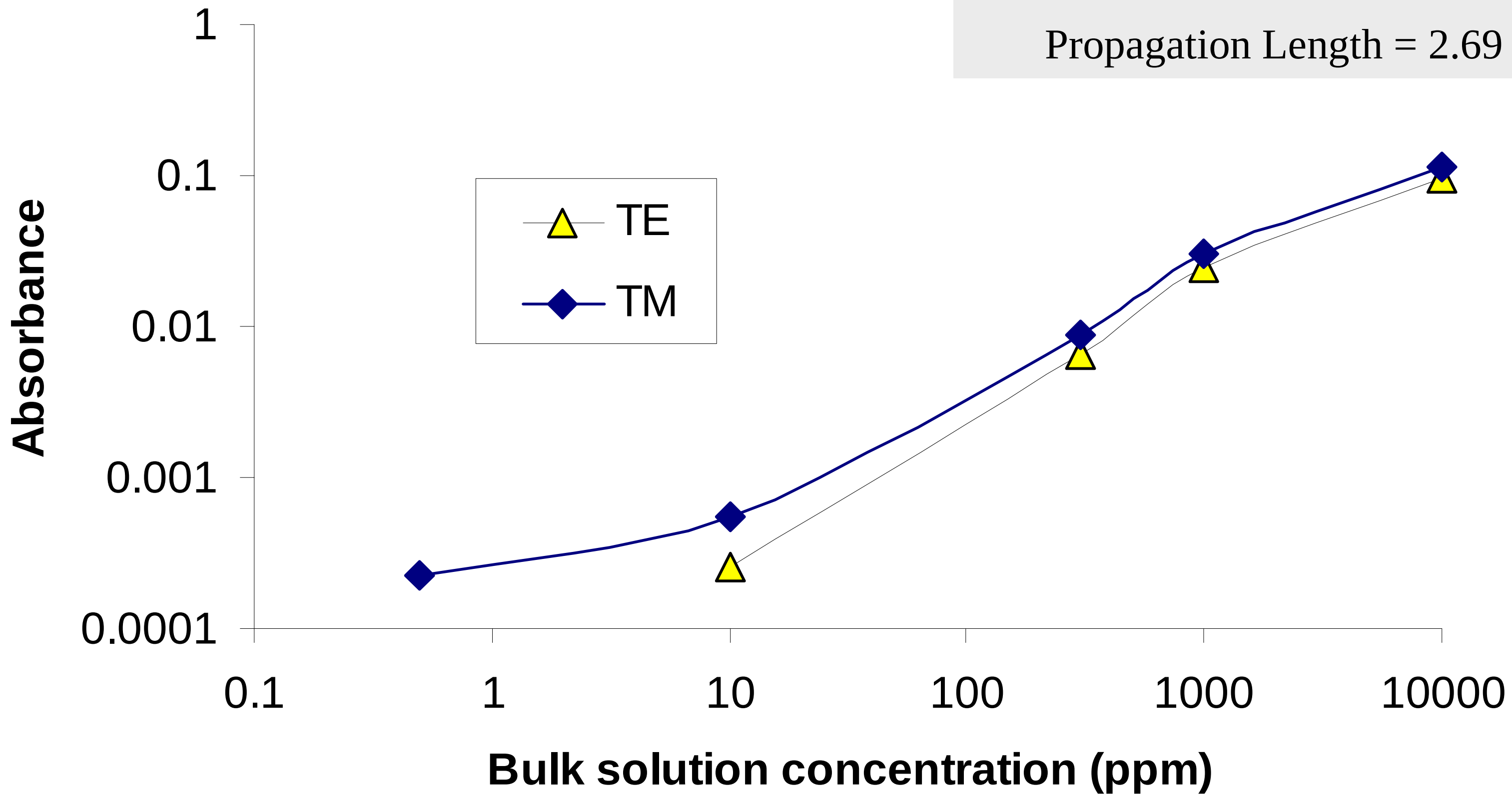


Experimental Curve for Cu^{2+} at the Silica Surface

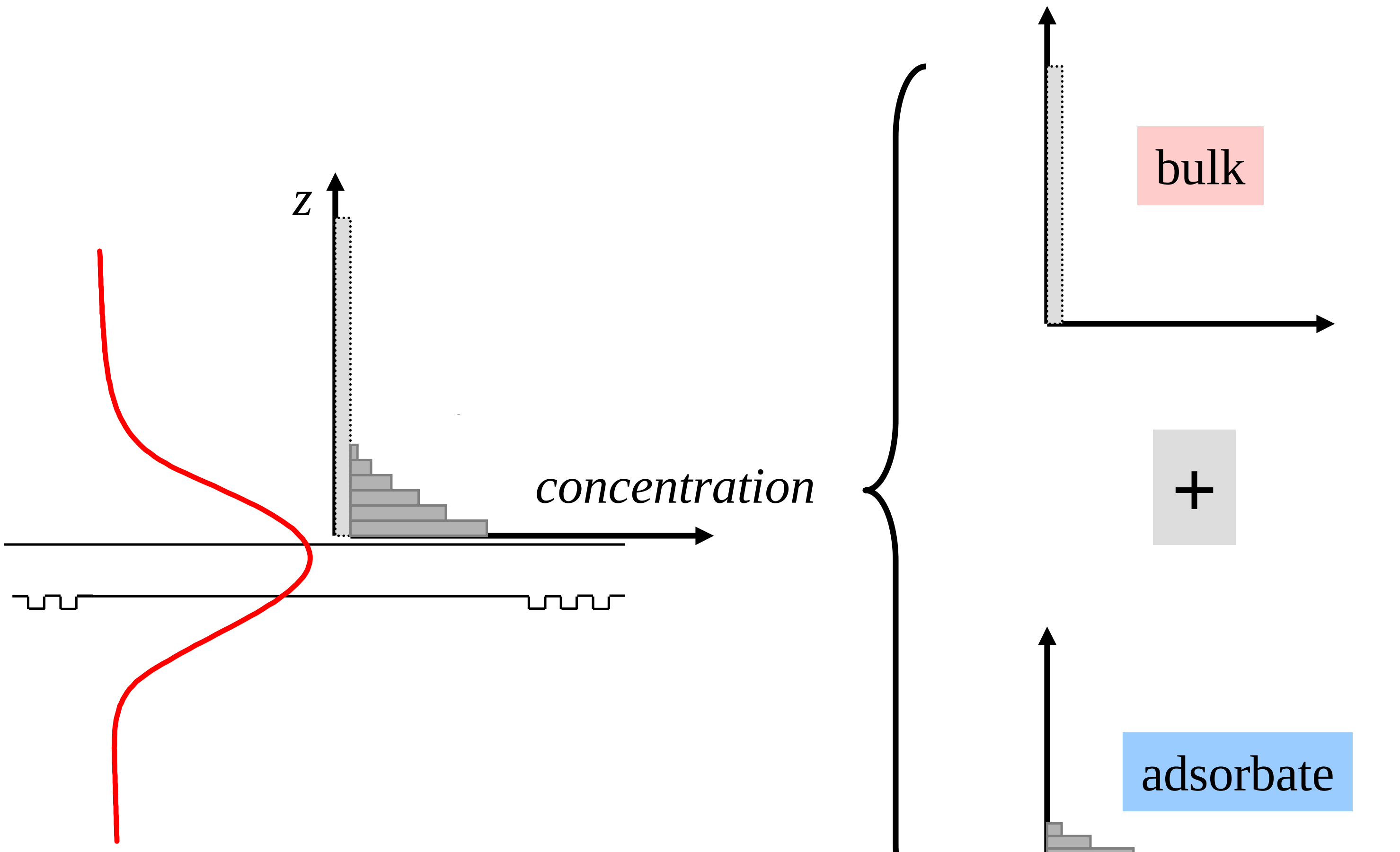
Analytical Wavelength = 820 nm

Molar Absorptivity = 11.2 $M^{-1}cm^{-1}$

Propagation Length = 2.69 cm



Signal = Bulk + Adsorbate



Data Analysis

TE mode

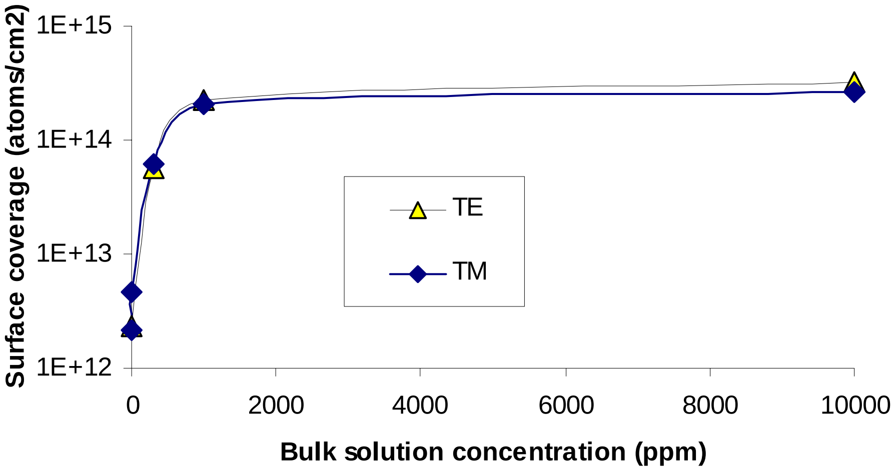
$$A_{\exp,TE} - A_{bulk,TE} = \varepsilon\ \sigma \left\{ \frac{2 n_l \left(n_w^2 - N_{TE}^2\right)}{t_{eff,TE}\ N_{TE} \left(n_w^2 - n_c^2\right)} L \right\}$$

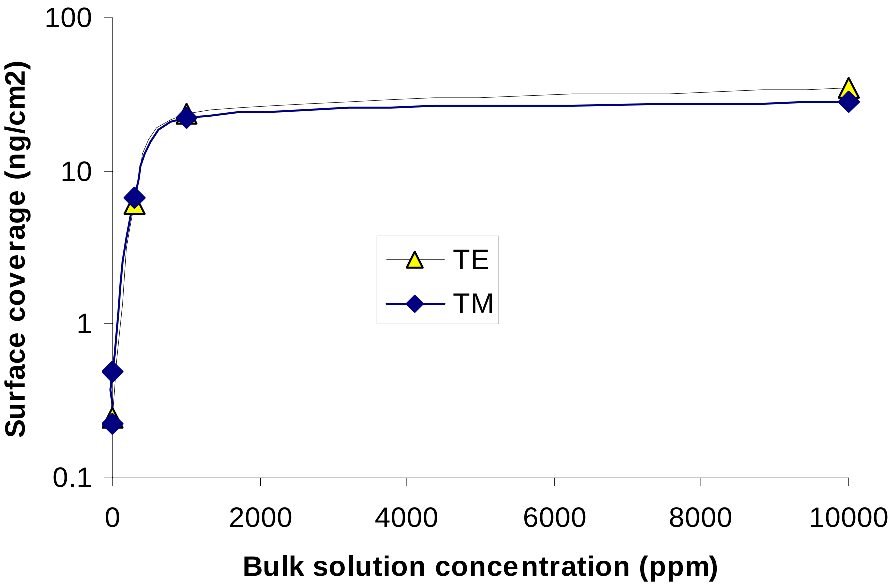
TM mode

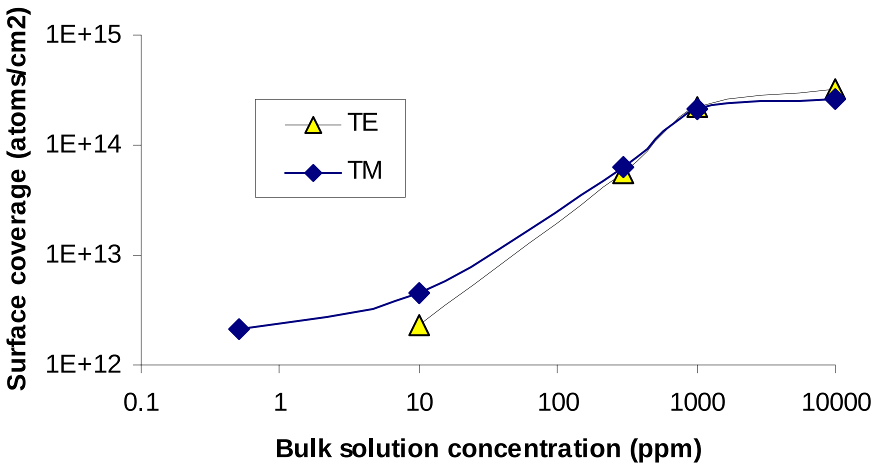
$$A_{\exp,TM} - A_{bulk,TM} = \varepsilon\ \sigma \left\{ \frac{2 n_l\ n_w^2 \left(n_w^2 - N_{TM}^2\right)\left[\left(1 + \left(n_c / n_l\right)^4\right) N_{TM}^2 - n_c^2\right]}{t_{eff,TM}\ N_{TM} \left[n_w^4 \left(N_{TM}^2 - n_c^2\right) + n_c^4 \left(n_w^2 - N_{TM}^2\right)\right]} L \right\}$$

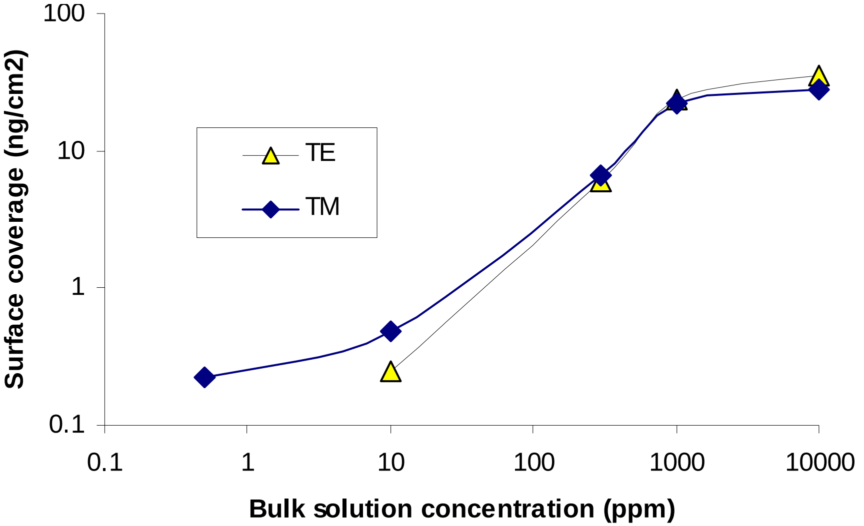
$$\sigma = Surface\ coverage$$

Surface coverage of Cu^{2+} at the Silica Surface









Ellipsometry

A User's Guide to Ellipsometry

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Mesa, Arizona

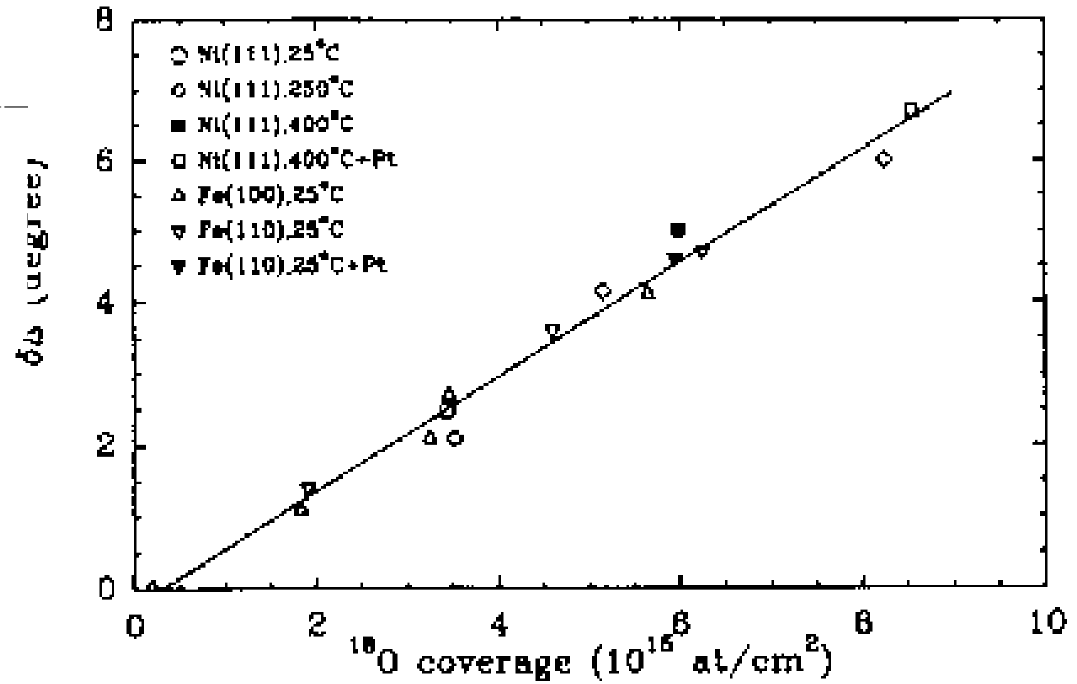


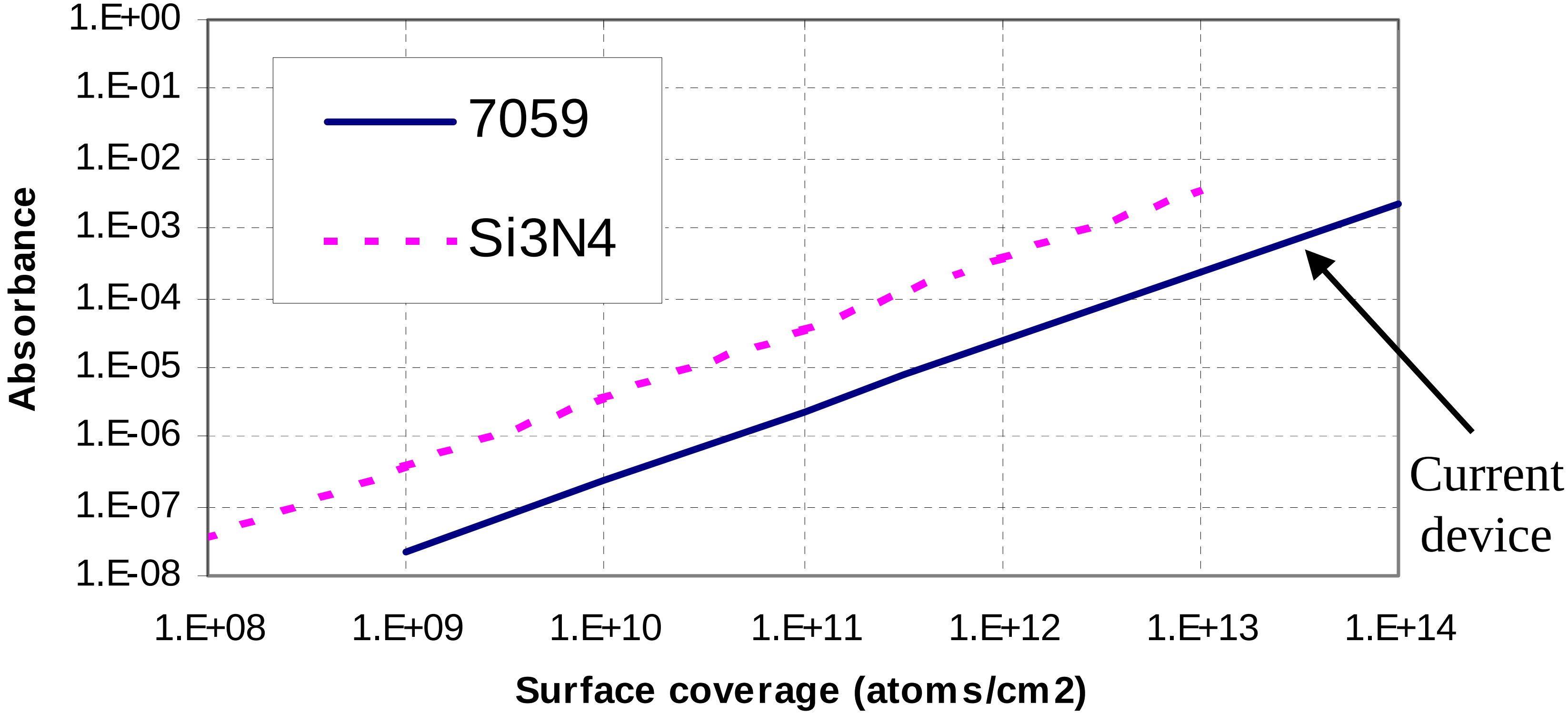
Figure 5-4. Ellipsometric parameter δΔ versus the absolute oxygen coverages on various surfaces of nickel and iron, both clean and covered with a small amount of platinum, as measured with the $^{18}O(p,\alpha)^{15}N$ nuclear reaction. The solid line is a least-squares fit to the data. (After Deckers[6])

Quartz Crystal Monitor (QCM)

- Resonant frequency ⟷ Mass load
- Detection limit : a few ng / cm^2
- Not chemically specific

Detection Limit for Different Waveguides

L = 1 cm



Summary

- Successfully developed an *in-situ* integrated optical probe to detect Cu^{2+} adsorbates at the silica-water interface

- Current sensitivity is 1/1000 of an atomic monolayer

On-going Work

- Enhance device sensitivity by:
  (a) improving waveguide mode confinement
  (b) increasing optical path length

- Perform measurement on metallic copper samples