Neutron Reflectometry as In Situ Probe of Thin Film Composition and Layer Structure for Investigating Corrosion and Hydrogen Absorption in Titanium

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About Neutrons

- A unique probe for materials and interfaces
- Spin = ½ (**magnetism**), Charge = 0 (**penetrating**)
- Half-life (outside atomic nucleus) = 611 s
- Thermal neutron velocity ~2200 m/s
- Thermal neutron wavelength ~ few Å (like **X-rays**)
- Thermal neutron energy ~27 **m**eV ($k_B T$)
- Neutron beam flux ~10^{14} /cm^2/s at **NRU** reactor core (Σ of all λ)
- Interacts with atomic nuclei via strong nuclear force
- Strength and direction (attractive/repulsive) of interaction are **independent of atomic number**
  - o depend on properties of nucleus
  - o **differ with isotope**

<u>Key parameter:</u> "coherent bound neutron scattering length"

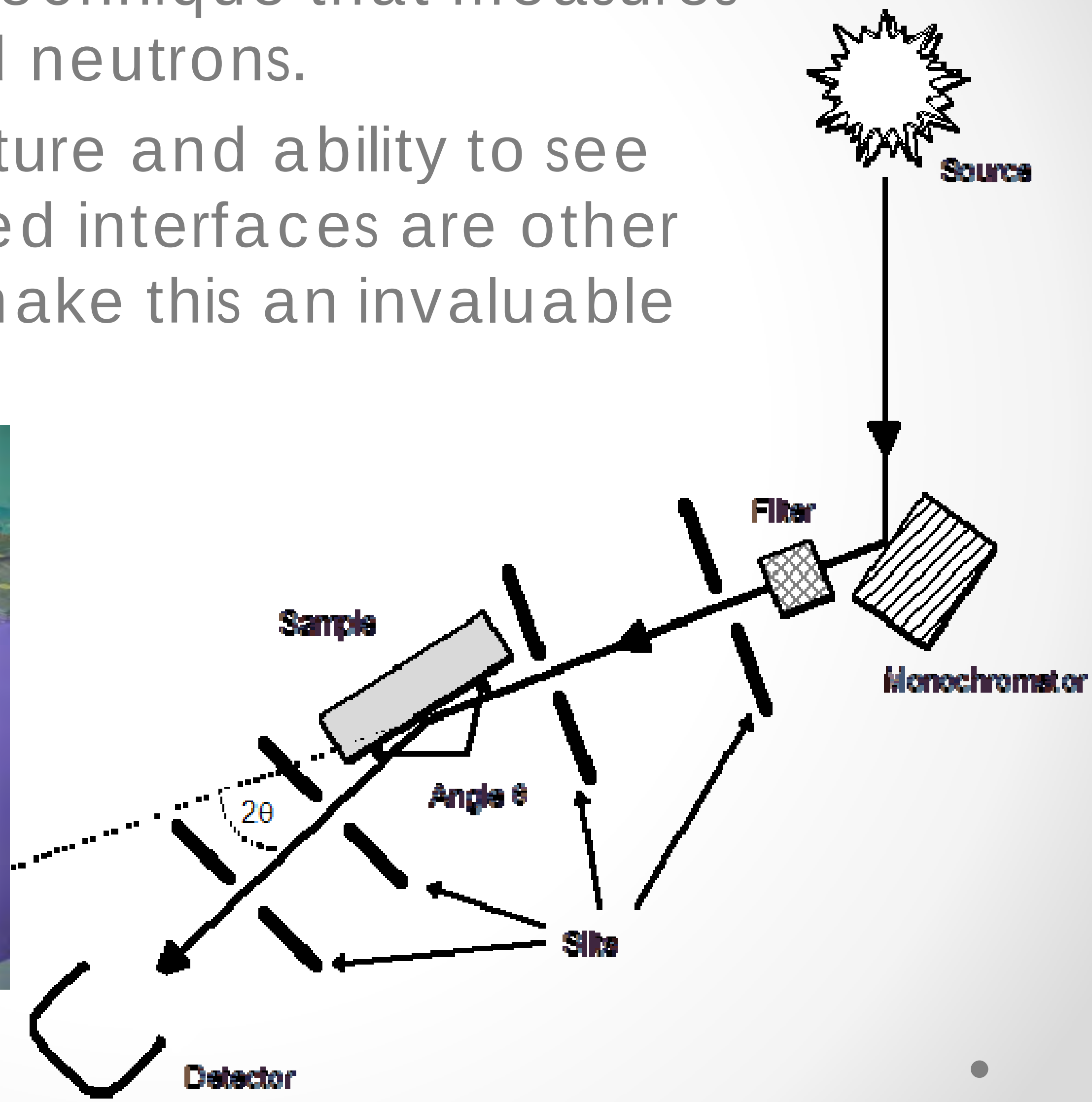
Neutron Scattering Lengths and Cross Sections

Isotope	(%) Abund.	(fm) **Coh b**	(fm) Inc b	(barn) Coh xs	(barn) Inc xs	(barn) Scatt xs	(barn) Abs xs
H	**---**	**-3.7390**	**---**	**1.7568**	**80.26**	**82.02**	**0.3326**
1H	99.985	-3.7406	25.274	1.7583	80.27	82.03	0.3326
2H	0.015	6.671	4.04	5.592	2.05	7.64	0.000519
3H	(12.32 a)	**4.792**	-1.04	2.89	0.14	3.03	0
O	**---**	**5.803**	**---**	**4.232**	**0.0008**	**4.232**	**0.00019**
16O	99.762	**5.803**	0	4.232	0	4.232	0.0001
17O	0.038	**5.78**	0.18	4.2	0.004	4.2	0.236
18O	0.2	**5.84**	0	4.29	0	4.29	0.00016
Ti	**---**	**-3.438**	**---**	**1.485**	**2.87**	**4.35**	**6.09**
46Ti	8.2	4.93	0	3.05	0	3.05	0.59
47Ti	7.4	3.63	-3.5	1.66	1.5	3.2	1.7
48Ti	73.8	-6.08	0	4.65	0	4.65	7.84
49Ti	5.4	**1.04**	5.1	0.14	3.3	3.4	2.2
50Ti	5.2	**6.18**	0	4.8	0	4.8	0.179

Neutron Reflectometry

- Surface analytical technique that measures specularly reflected neutrons.
- Non-destructive nature and ability to see hydrogen and buried interfaces are other rare qualities that make this an invaluable technique.

“D3” reflectometer at Chalk River



Reflectivity Fundamentals

- From Snell and Fresnel:

$$R = \left|\frac{n_0 \sin\theta_0 - n_1 \sin\theta_1}{n_0 \sin\theta_0 + n_1 \sin\theta_1}\right|^2$$

- Neutron refractive index determined by ρb, the "scattering length density" (SLD)
- SLD of mixtures by simple weighted average:

$$\rho b = \sum_i \rho_i b_i$$

- Momentum transfer: $Q = \frac{4\pi}{\lambda}\sin\theta$
- Neutron reflectivity (within Born Approximation):

$$R(Q) = \frac{16\pi^2}{Q^2}\left|\int \rho b(z) e^{-iQz} dz\right|$$

What Do We Get from Neutron Reflectometry?

- Intensity profile of reflectivity yields composition of surface layers.

$$Q_c^2 = 16\pi\rho b$$

where Q_c is the critical momentum transfer for total external reflection

- b may be + or – (e.g., b_H = -3.7 fm, but b_D = 6.7 fm).
- If b < 0, then Q_c is imaginary (and therefore unobservable)
-

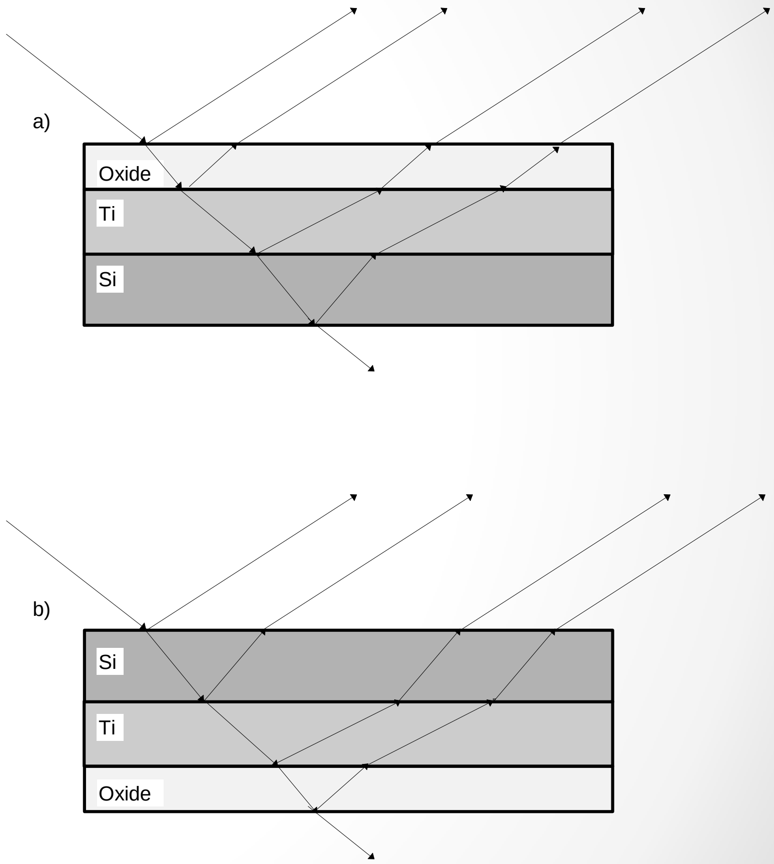
Element, Compound, or Functional Group	(Effective) Coherent Neutron Scattering Length[a], b (fm)	Number Density[b], ρ (Å^{-3})	SLD, ρb (Å^{-2})
Si	4.1491	4.996×10^{-2}	2.07×10^{-6}
Ti	-3.438	5.670×10^{-2}	-1.95×10^{-6}
O	5.803	N/A	N/A
H	-3.7390	N/A	N/A
Na	3.63	N/A	N/A
Cl	9.5770	N/A	N/A
Fe	9.45	N/A	N/A
H_2O	-1.675	3.343×10^{-2}	-0.56×10^{-6} @ 20°C
SiO_2 (cristobalite)	15.7551	2.325×10^{-2}	3.66×10^{-6}
SiO_2 (amorphous)	15.7551	2.205×10^{-2}	3.47×10^{-6}
SiO_2 (quartz)	15.7551	2.666×10^{-2}	4.20×10^{-6}
TiO_2 (rutile)	8.168	3.211×10^{-2}	2.62×10^{-6}
TiO_2 (anatase)	8.168	2.894×10^{-2}	2.40×10^{-6}
TiO_2 (brookite)	8.168	3.143×10^{-2}	2.56×10^{-6}
TiH_2	-10.916	4.705×10^{-2}	-5.14×10^{-6}
-OH group	2.064	N/A	N/A
Air	~17	$\sim 2.5 \times 10^{-5}$	Negligible

What Else Can We Get from Neutron Reflectometry?

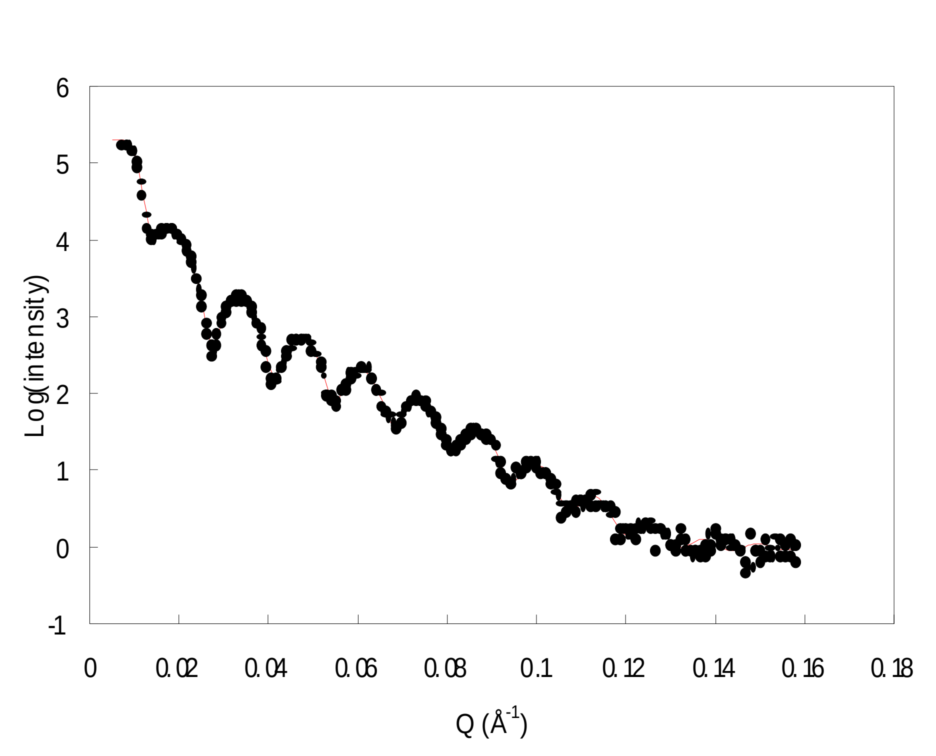
- Difference in path lengths of coherent neutron beam results in interference at the detector.
- Interference pattern allows determination of layer thickness (0.5-300 nm) using Bragg's Law.

$$2d \sin \Theta = \lambda$$

- Can see buried interfaces too.



But How Do We Actually Get Sample Composition and Thickness?

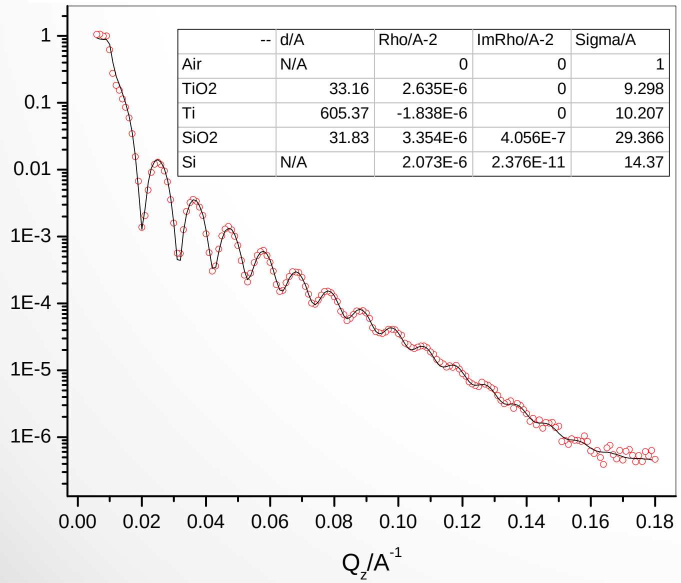


- Raw data in momentum space are modeled to yield a real space profile.
- Model is proposed based on other knowledge, then refined by a least squares fitting process.

Example: Ti Thin Film

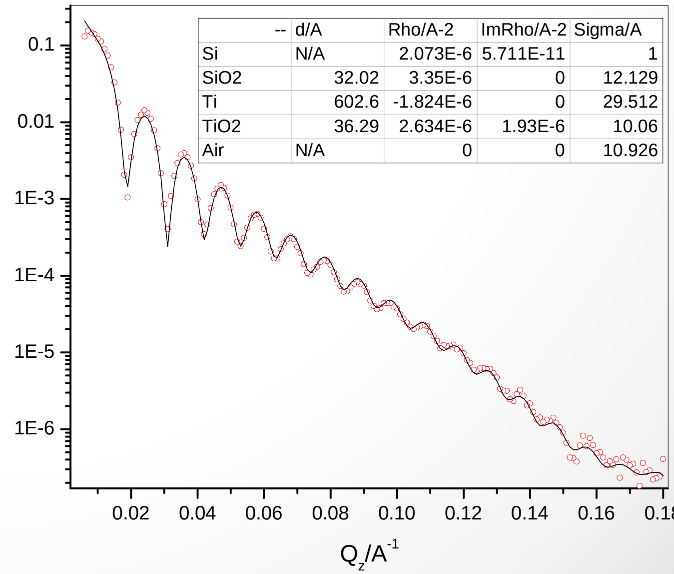
- Thin film of Ti deposited on Si single crystal substrate
  - Si because it is very flat, transparent to neutrons
  - Ti film ~ 50 nm thick (covered with a few nm of native oxide)
  - Magnetron sputtering yields flat Ti film, uniform thickness
  - Sample size ~ 100 mm   Big, eh? Glancing angle = large beam footprint.
  - Scan with neutrons incident on Ti from air side then from Si side.

Neutrons incident from air



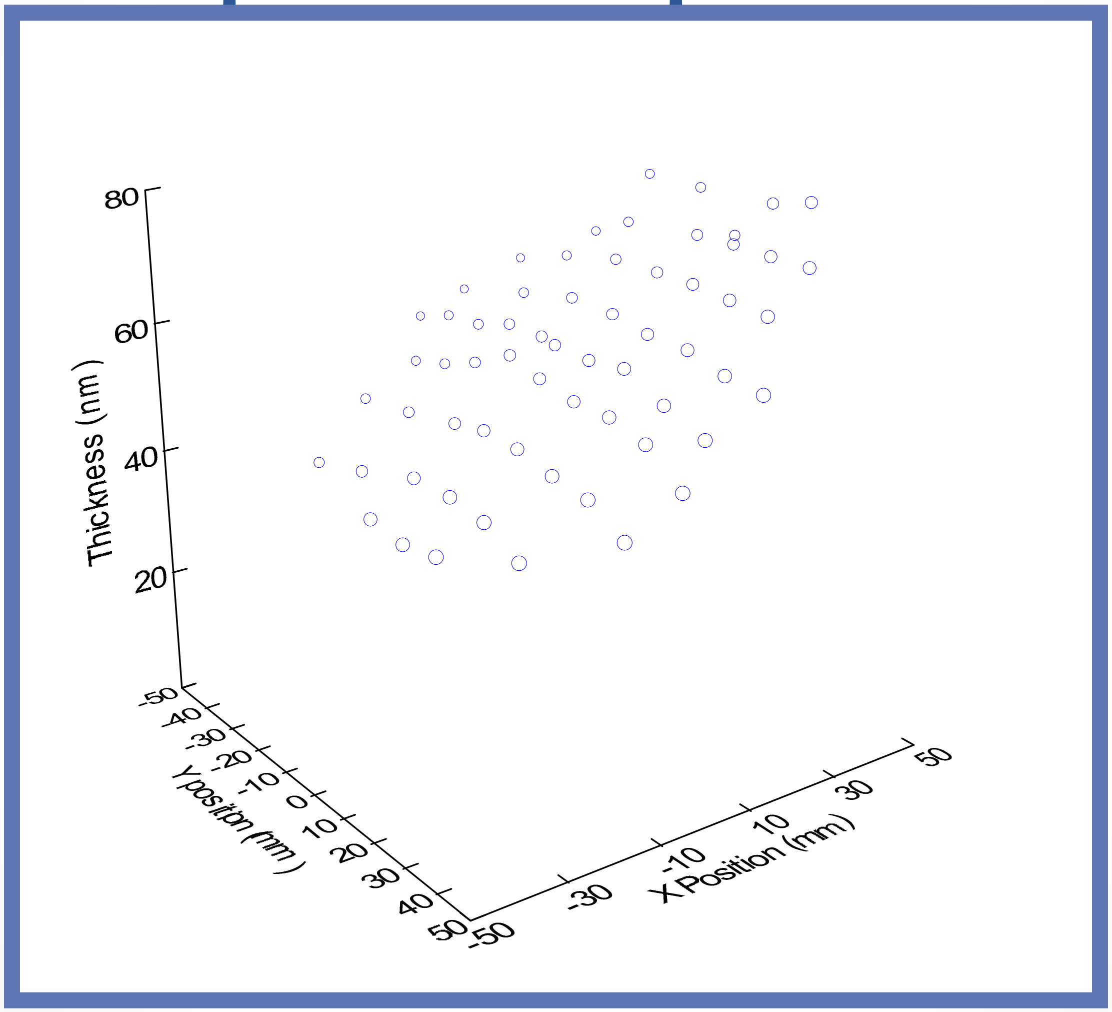
--	d/A	Rho/A-2	ImRho/A-2	Sigma/A
Air	N/A	0	0	1
TiO2	33.16	2.635E-6	0	9.298
Ti	605.37	-1.838E-6	0	10.207
SiO2	31.83	3.354E-6	4.056E-7	29.366
Si	N/A	2.073E-6	2.376E-11	14.37

Neutrons incident from Si



--	d/A	Rho/A-2	ImRho/A-2	Sigma/A
Si	N/A	2.073E-6	5.711E-11	1
SiO2	32.02	3.35E-6	0	12.129
Ti	602.6	-1.824E-6	0	29.512
TiO2	36.29	2.634E-6	1.93E-6	10.06
Air	N/A	0	0	10.926

Sample Preparation



Sample must be flat, uniform, LARGE

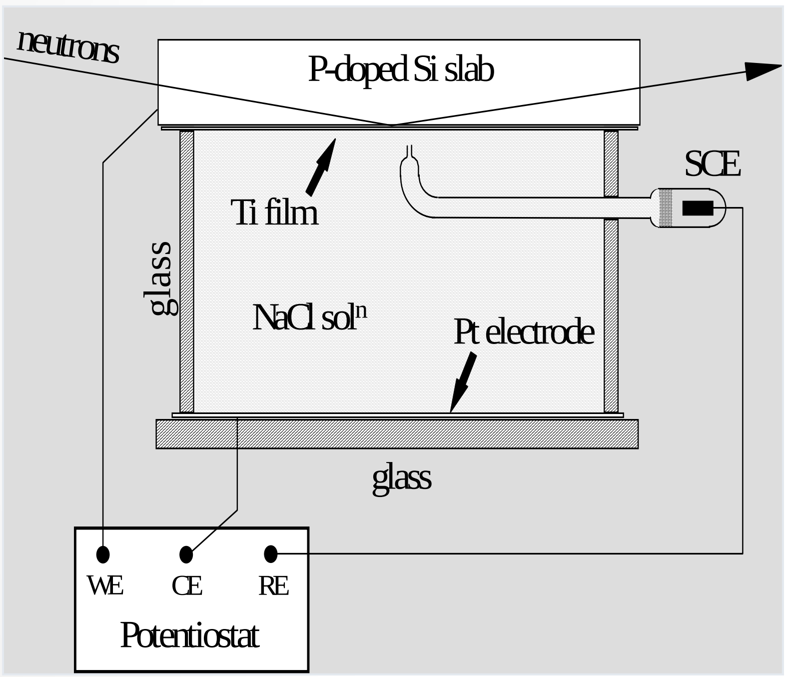
Approach

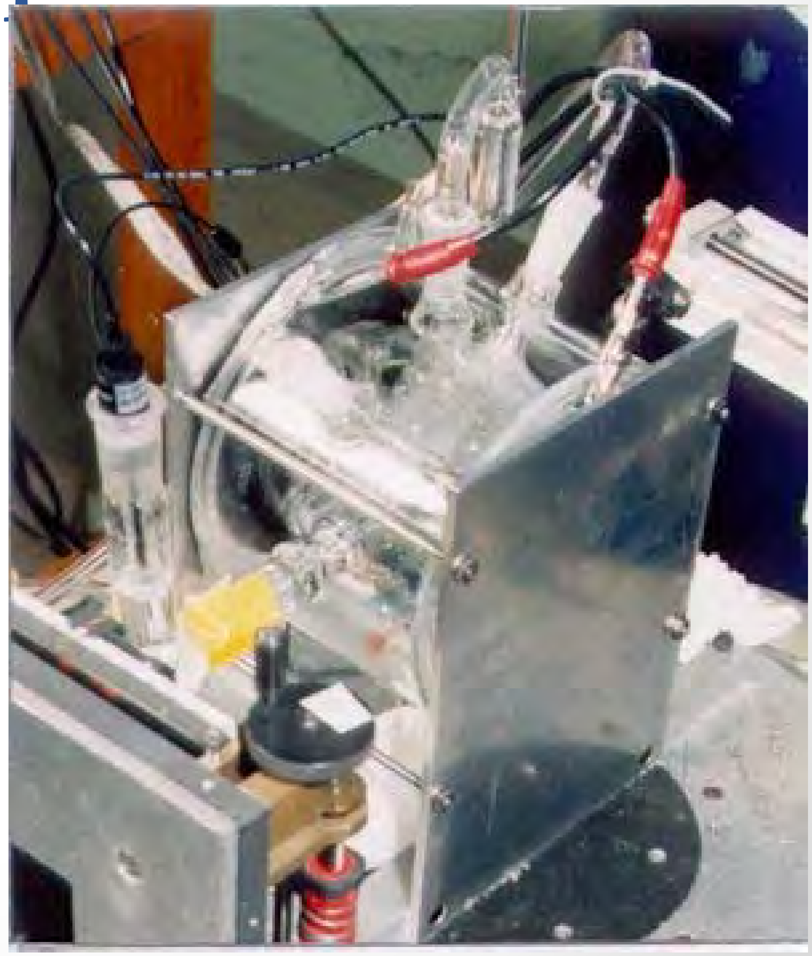
- We used a combination of electrochemical techniques and neutron reflectometry to probe anodic oxide film growth on Ti and then hydrogen absorption by cathodically polarized Ti.
- Neutron reflectometry is easily performed in situ with samples in various environments, including electrodes in solution under electrochemical control.

Experimental

- Pure Ti film, ~500 Å
- Sputtered on 4” Si slab
- Electrolyte solution 0.27 mol/L NaCl
- Neutral pH, Argon deaerated
- SCE reference electrode
- Neutron scans on dry sample, then in cell at E_{oc} and under potentiostatic control at a series of more positive potentials to thicken oxide film.
- Next, neutron scans during application of a series of more negative potentials to produce hydrogen from water.
- Electrochemical impedance spectroscopy (EIS) recorded during neutron scans.

In Situ Electrochemistry/ Neutron Reflectometry Setup

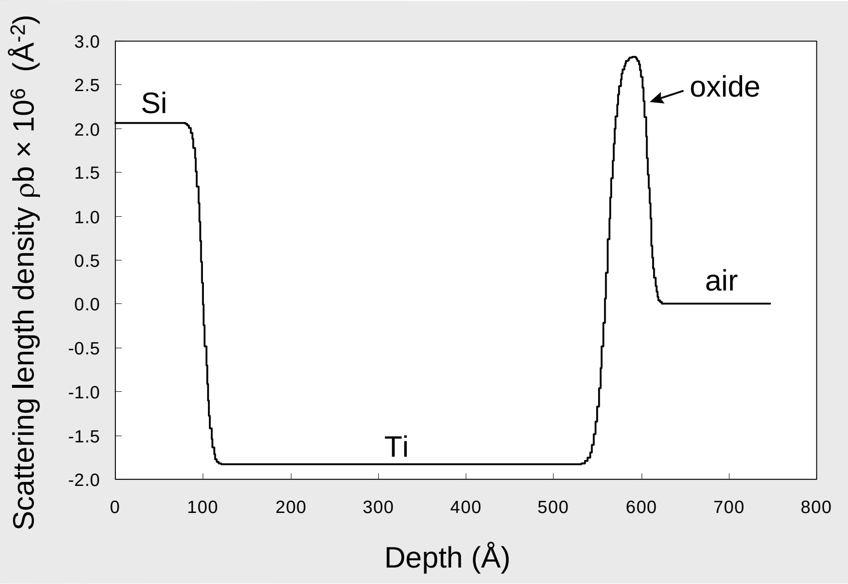




In situ reflectometry.

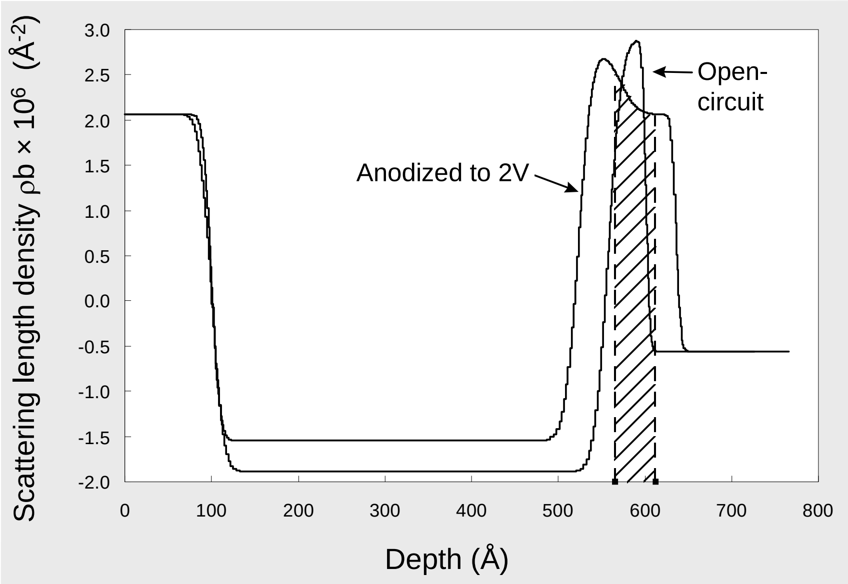
Neutrons enter from the back.

Real Space Profiles



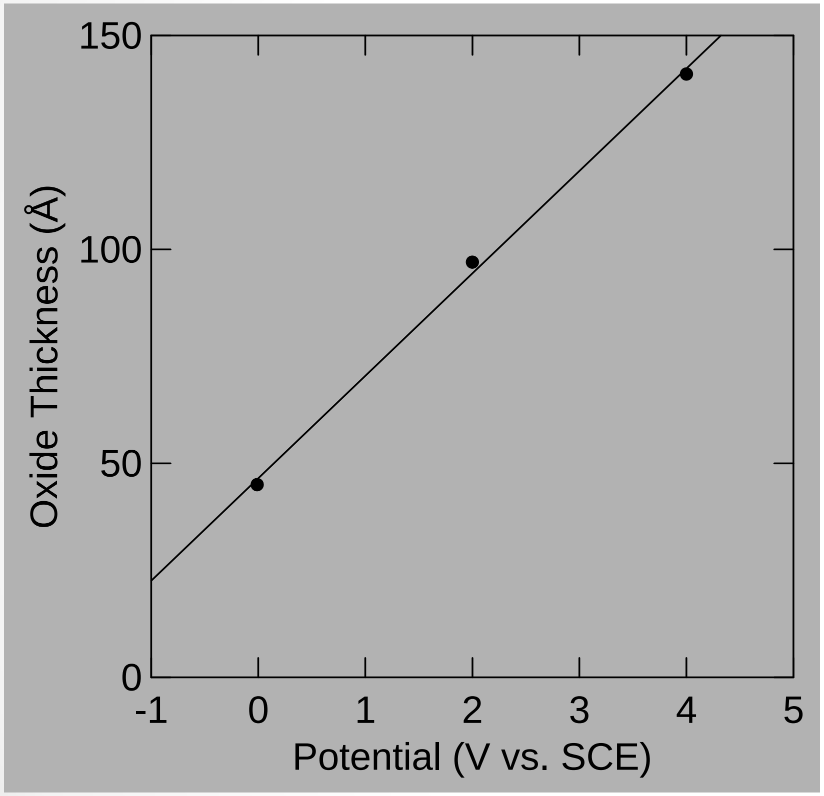
- As-prepared film on Si in air, with 461 Å of Ti metal and 47 Å of rutile-like oxide
- Note the negative SLD of Ti

- No change upon immersion in 0.27 M NaCl (H_2O) at E_{oc}.
- Upon anodization to 2 V:
- Metal thins (38Å), oxide thickens (65 Å).
- $\Re_{PB} = 1.72$
- Bilayer oxide formed.



Oxide Film Growth

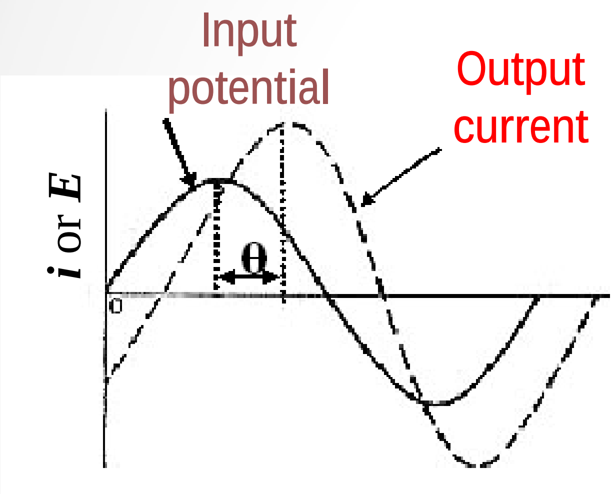
Titanium



Oxide layer growth (and corresponding thinning of the metal layer) is consistent with the Pilling-Bedworth ratio measured by other means. Shows that no Ti is lost to dissolution (within the resolution of this technique).

α = 25 Å/V

Electrochemical Impedance Spectroscopy



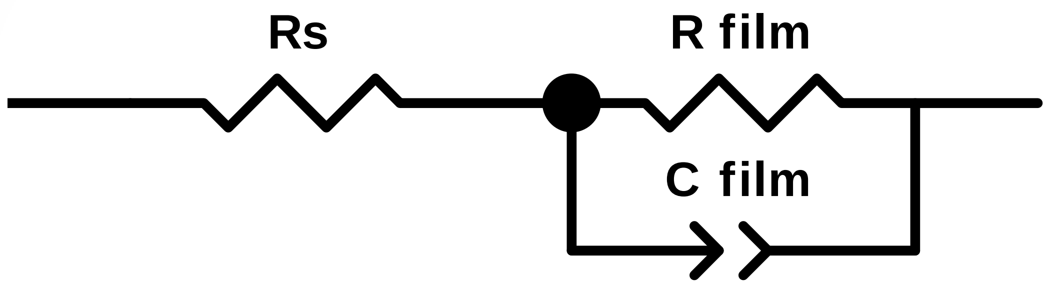
Sinusoidal potential input yields phase-shifted sinusoidal current output

Impedance (Z) is obtained using expression analogous to Ohm's Law

$$Z = \frac{E(t)}{I(t)} = Z_o \frac{\sin(\omega t)}{\sin(\omega t + \theta)}$$

Z as a function of the sinusoidal frequency is modeled using electrical equivalent circuits consisting of passive circuit elements (resistors, capacitors, etc.)

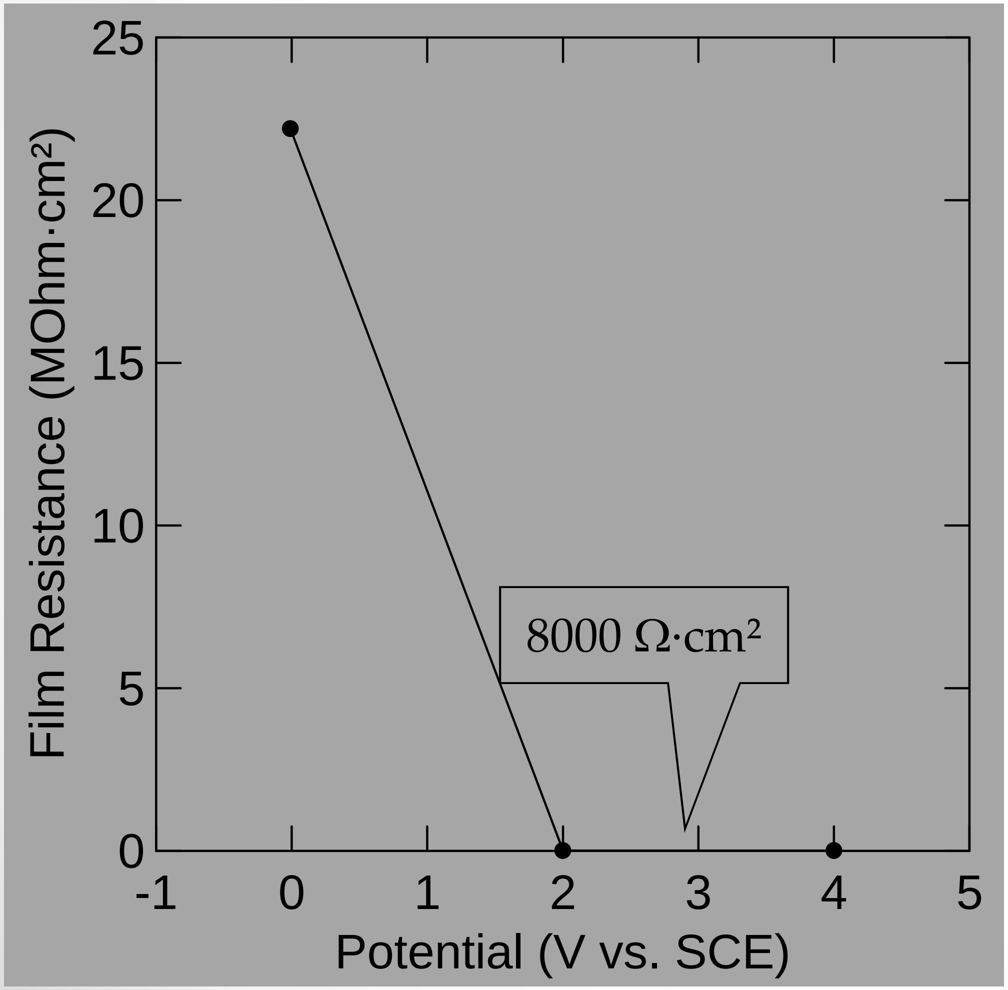
Electrochemical Impedance Spectroscopy Modeling

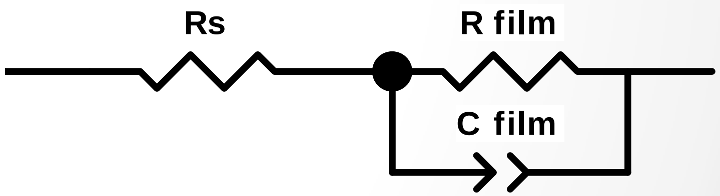


Simple equivalent circuit with one time constant fit EIS spectra from anodically and cathodically polarized Ti.

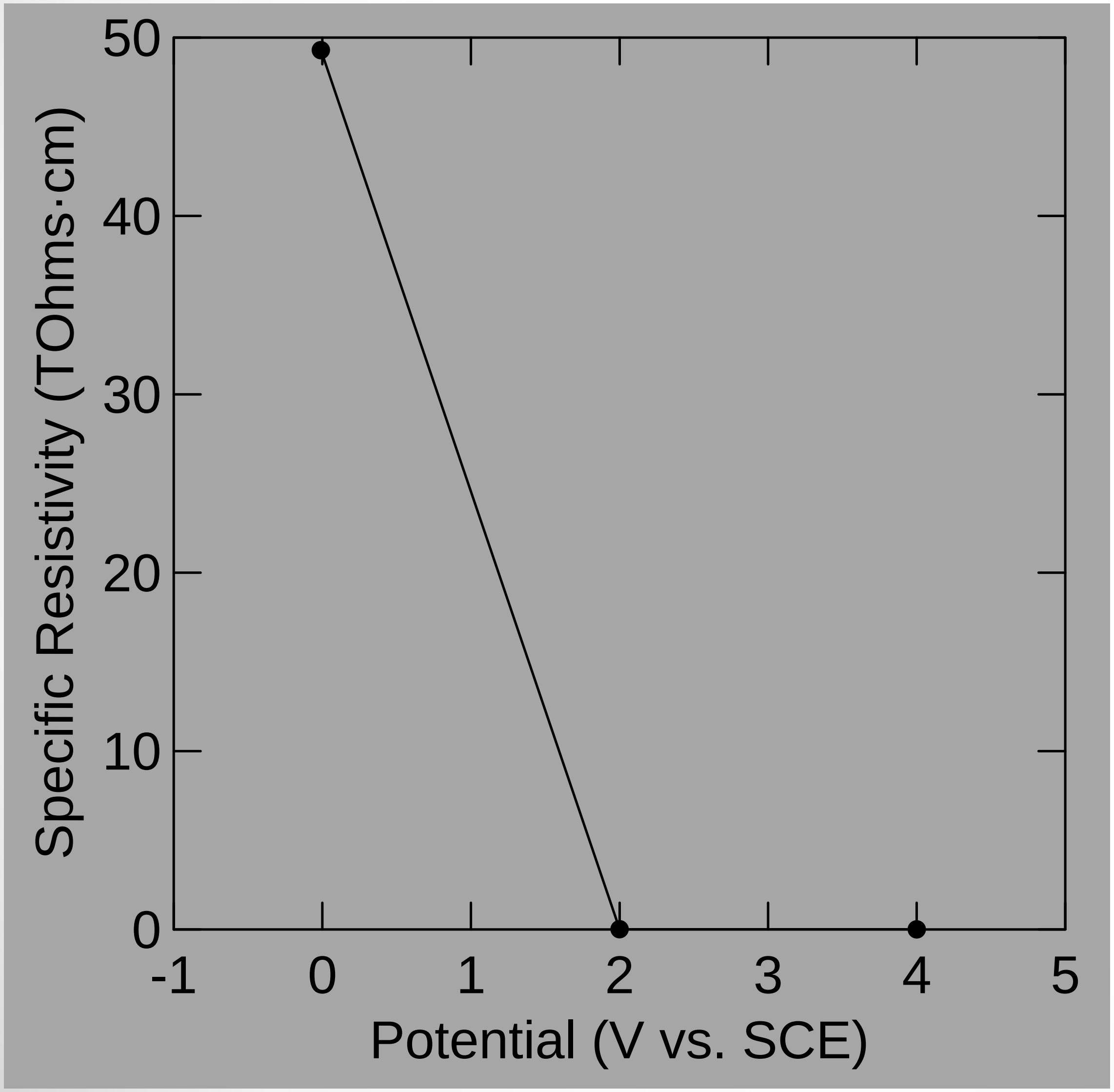
Constant phase element accounts for non-ideal capacitance.

From In Situ EIS



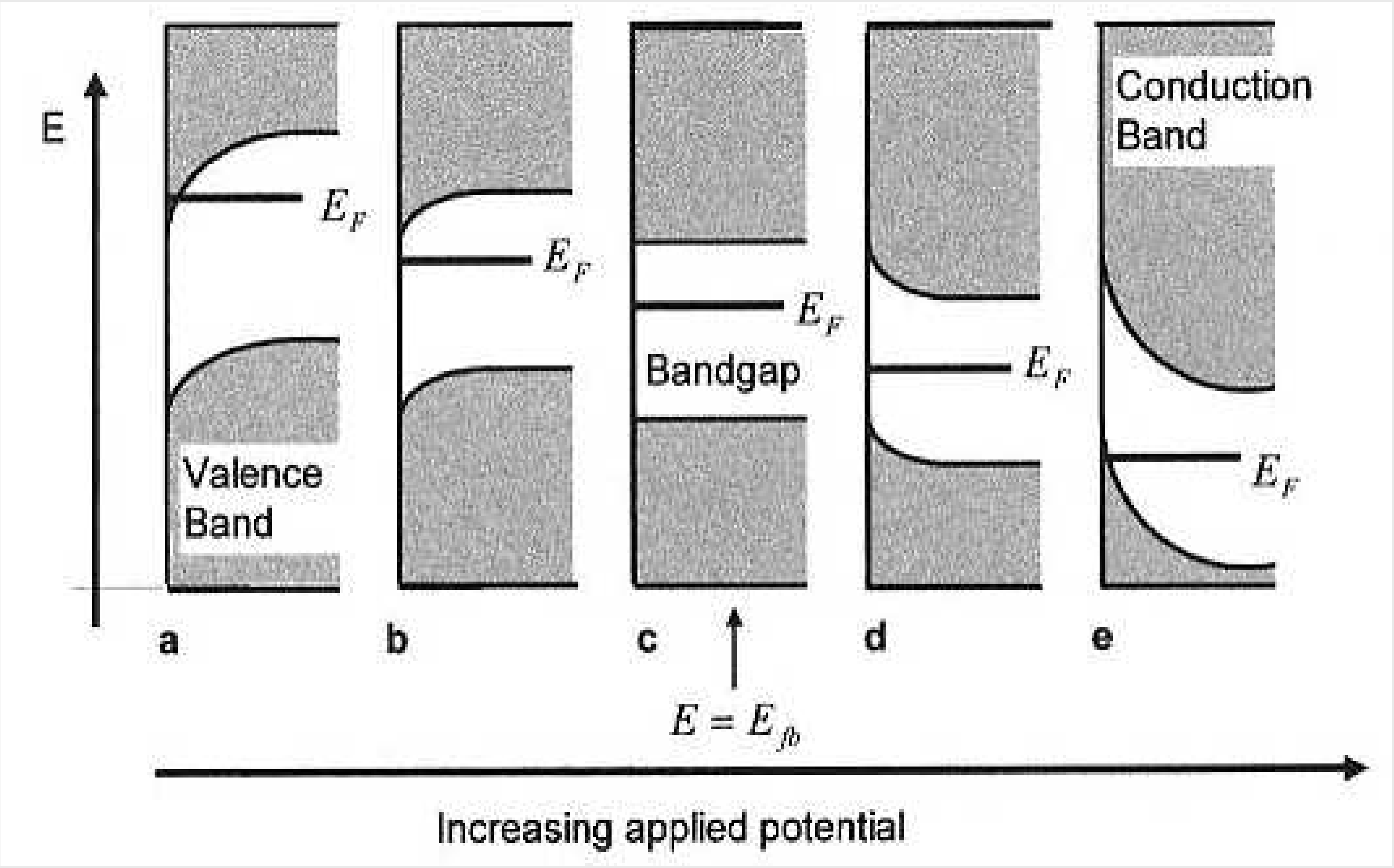


Specific Resistivity

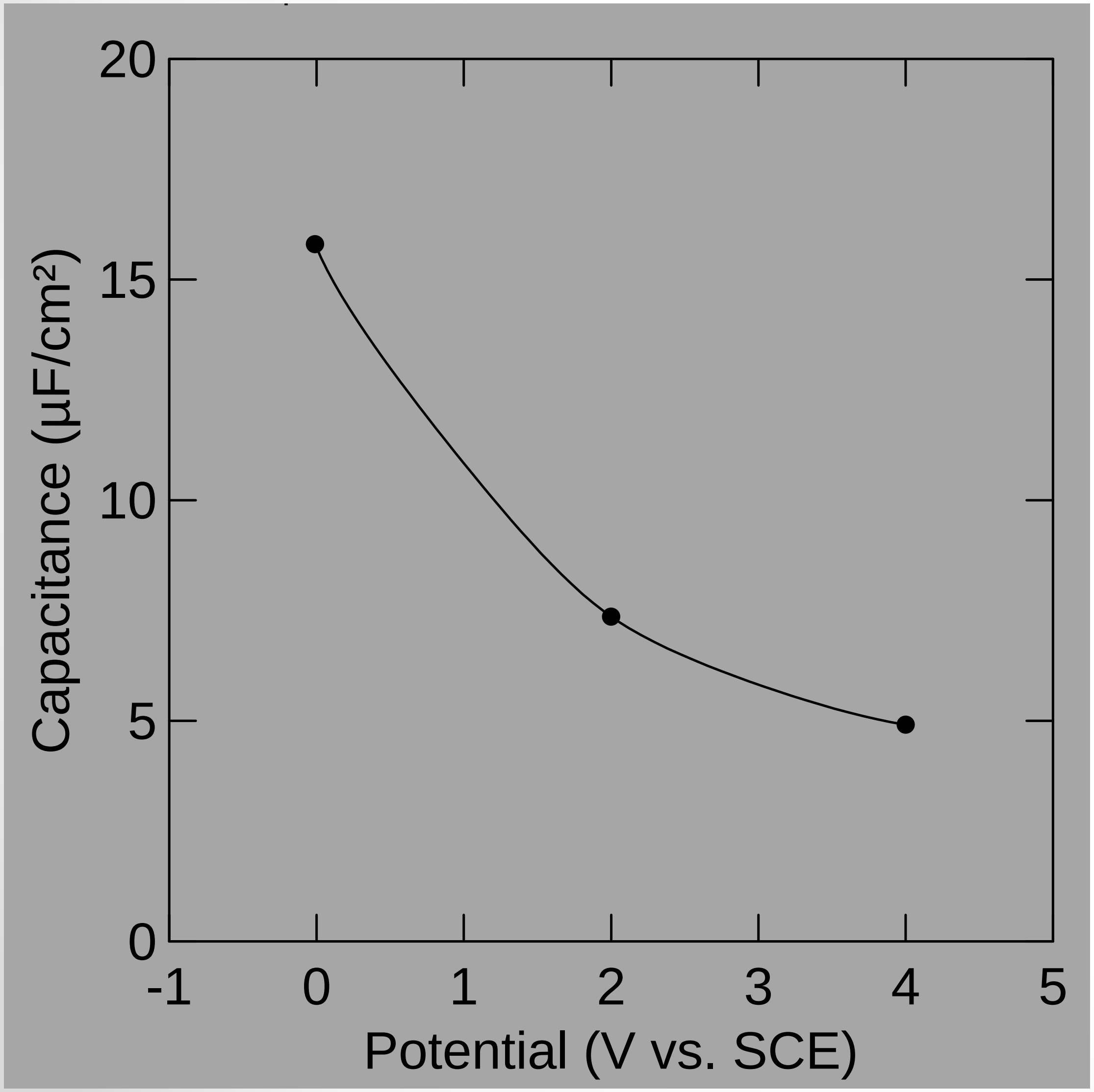


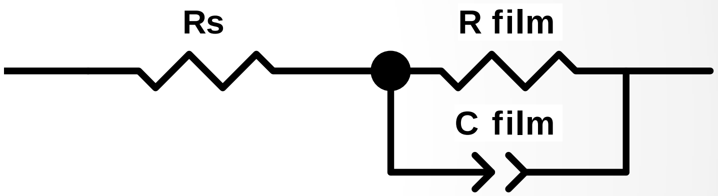
Resistivity =
Resistance/Thickness

Band Bending During Polarization

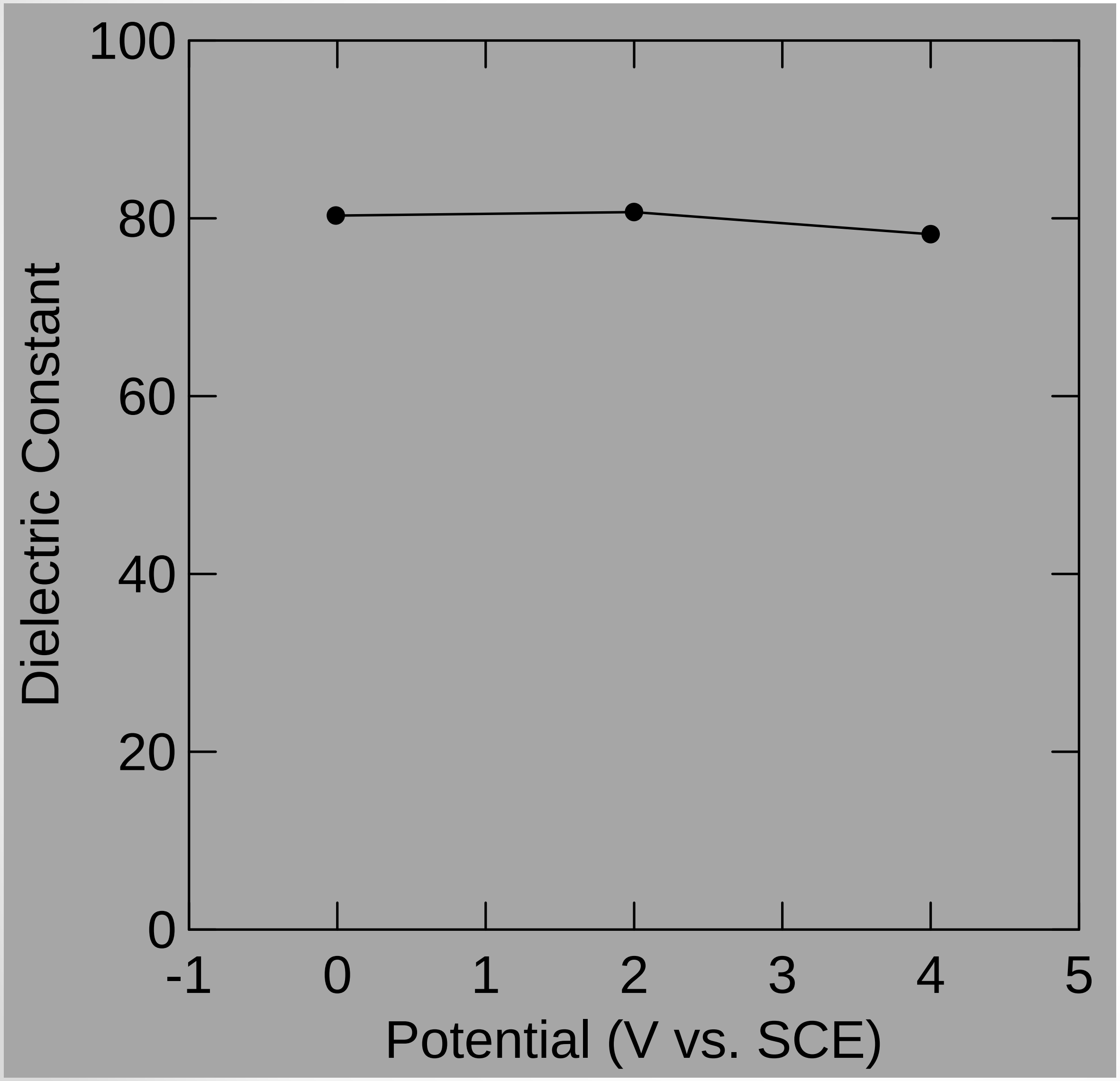


Film Capacitance



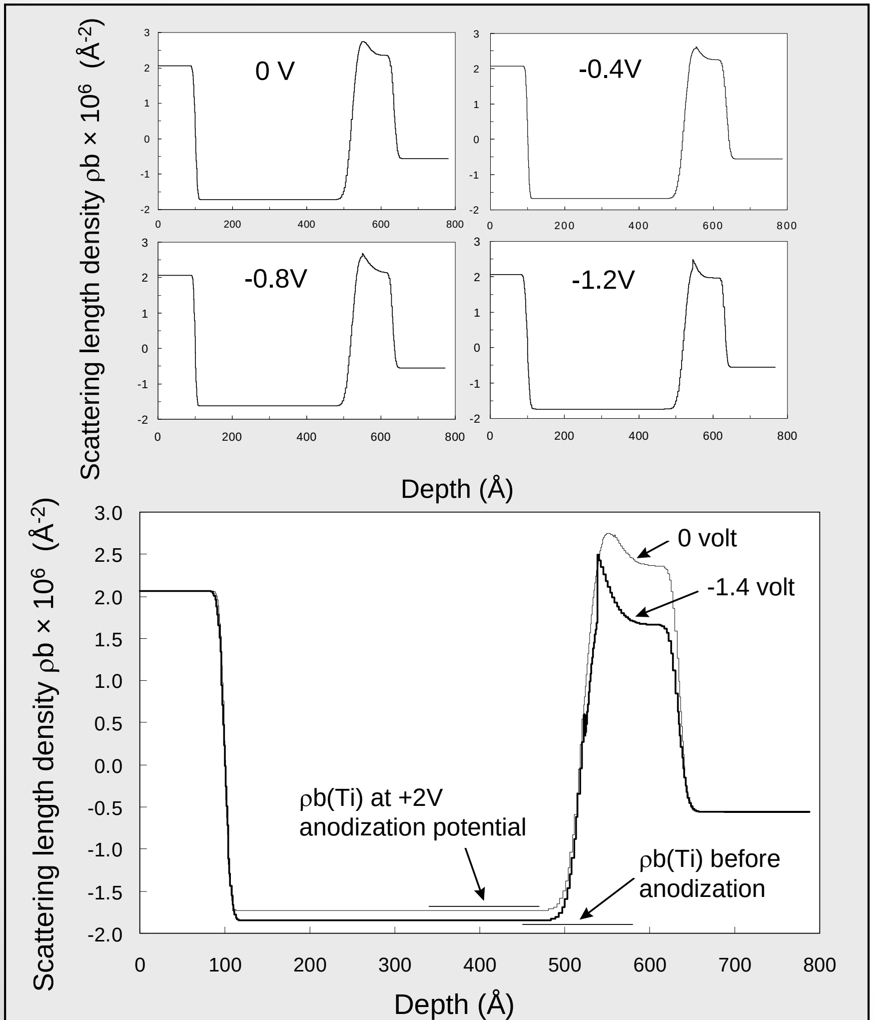


Dielectric Constant



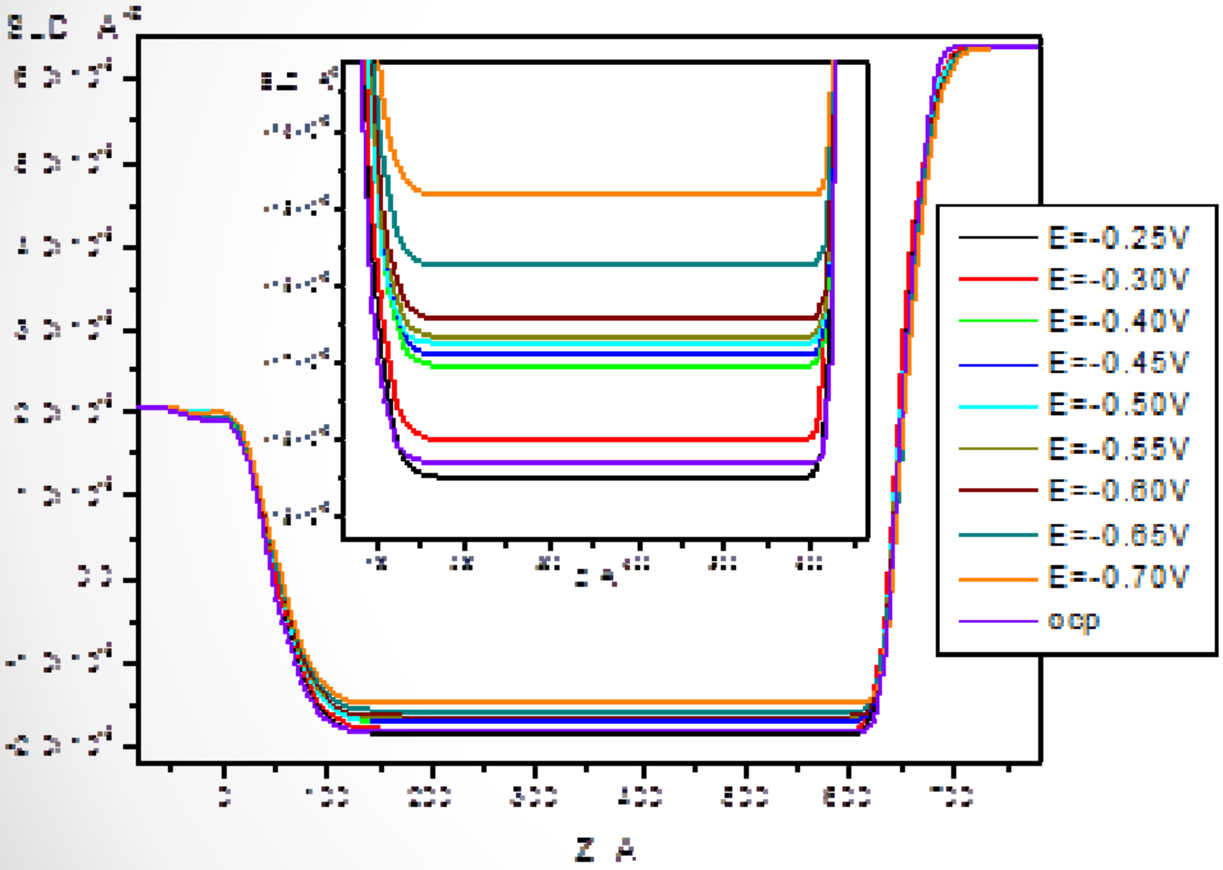
$$\varepsilon = \frac{Cd}{\varepsilon^\circ}$$

Reflectivity Profiles During Cathodic Polarization



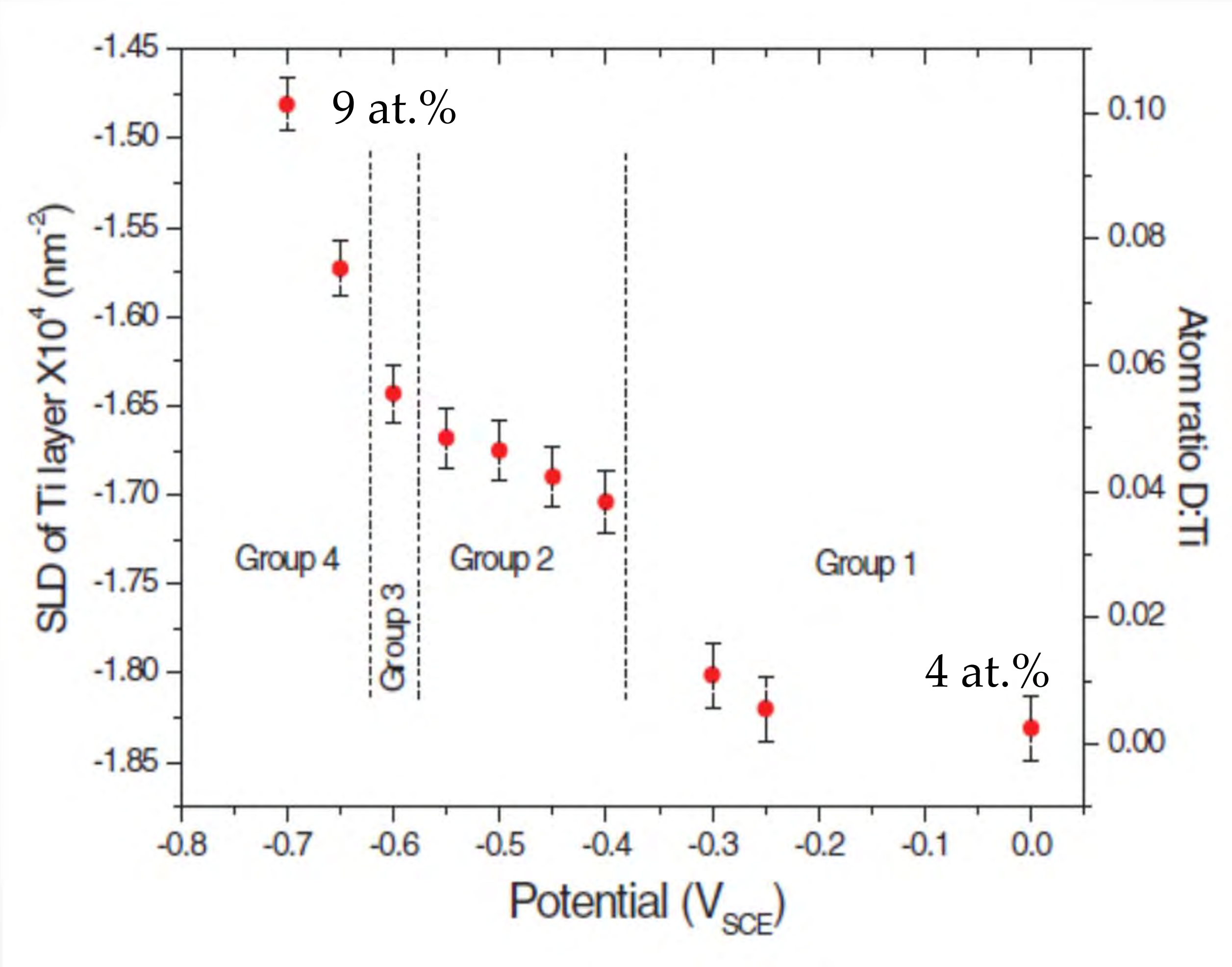
- SLD of outer layer of oxide decreases
- Outer layer broadens, inner layer thins
- Overall oxide layer thickness constant
- Metal layer SLD decreases again
- Changes due to H absorption
- Oxide converted to $TiO_2 \cdot H_2O$ (or $TiO(OH)_2$)

Hydrogen Absorption into Ti



- Unanodized Ti film in 0.27 M NaCl (in D_2O)
- Polarized to successively lower E, held for ~16 h.
- Sudden jump in H content between -300 mV and -400 mV, and again between -600 mV and -650 mV, consistent with previous results (Shibata and Zhu, Noël, Zeng).

Hydrogen Content



Conclusions

- Neutron reflectometry provides quantitative layer thickness and composition information, including H content.
- Reflectometry can be performed in situ while electrochemical treatments are applied or electrochemical measurements are being made.
- Coupled measurements yield information unobtainable from individual measurements (e.g., resistivity, dielectric constant)
- Conclusions based on observation of H could (should) be verified by repeating using D.
-

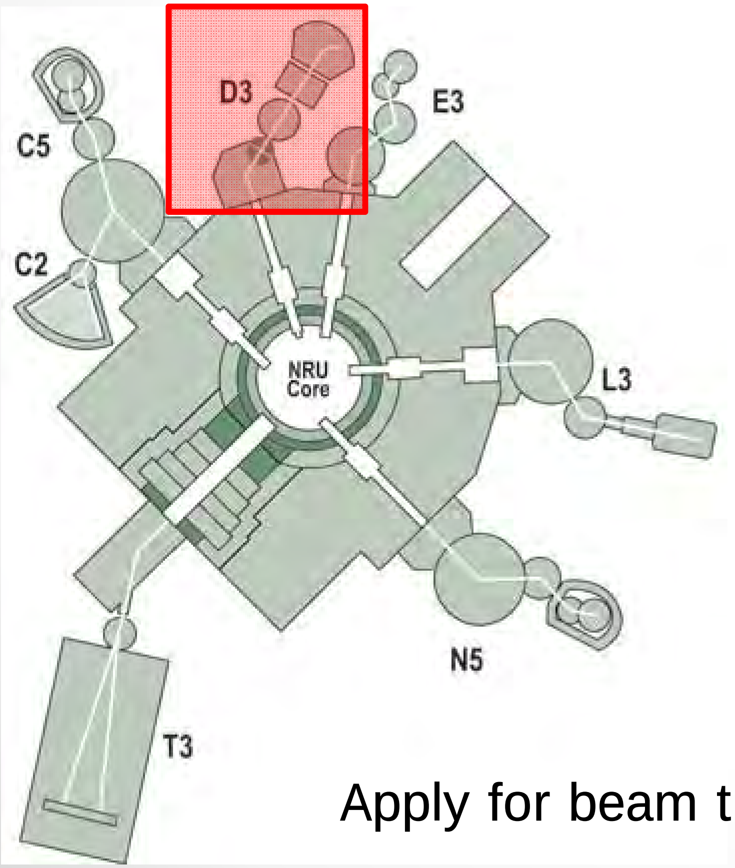
Acknowledgements:
Canadian Neutron Beam Centre
NSERC
UWO NanoFab Lab

Accessing Neutrons:

- Write a research proposal (a neutron geek will help you)!
- Go to a neutron beam facility:
  - o Spallation Neutron Source, Oak Ridge National Lab, Oak Ridge, TN
  - o NIST Center for Neutron Research, NIST, Gaithersburg, MD
  - o Lujan Center, Los Alamos Neutron Science Center, Los Alamos, NV
  - o ISIS Neutron Source, Rutherford Appleton Laboratory, UK
  - o Institut Laue-Langevin, Grenoble, France
  - o Canadian Neutron Beam Centre, Chalk River, ON
  - o Bragg Institute, ANSTO, Lucas Heights, Australia
  - o Etc…….
- **Access** and **help** are **free** if you publish.
- Travel support often available for students
- **You work with an instrument scientist who knows neutron physics and how to operate the machine** –you bring samples, a problem to answer and your expertise. Analyze data and write paper together.
- Ancillary equipment/facilities available (labs, cells, cryostats, magnets, heaters, etc.)
- International labs also accessible.

Accessing Neutrons

- In Canada, Canadian Neutron Beam Centre, NRU Reactor, Chalk River, Ontario.
- Access on basis of peer-reviewed proposal.



C2 High Resolution Powder Diffractometer
C5 Polarized Beam Triple-Axis Spectrometer
D3 Reflectometer
E3 Triple-axis Spectrometer
L3 Stress-Scanning Diffractometer
N5 Triple-Axis Spectrometer
T3 Image-Plate Diffractometer

Apply for beam time http://www.cins.ca/beam.html

Acknowledgements

Dave Shoesmith and Clara Wren, UWO

Jared Smith, CNL

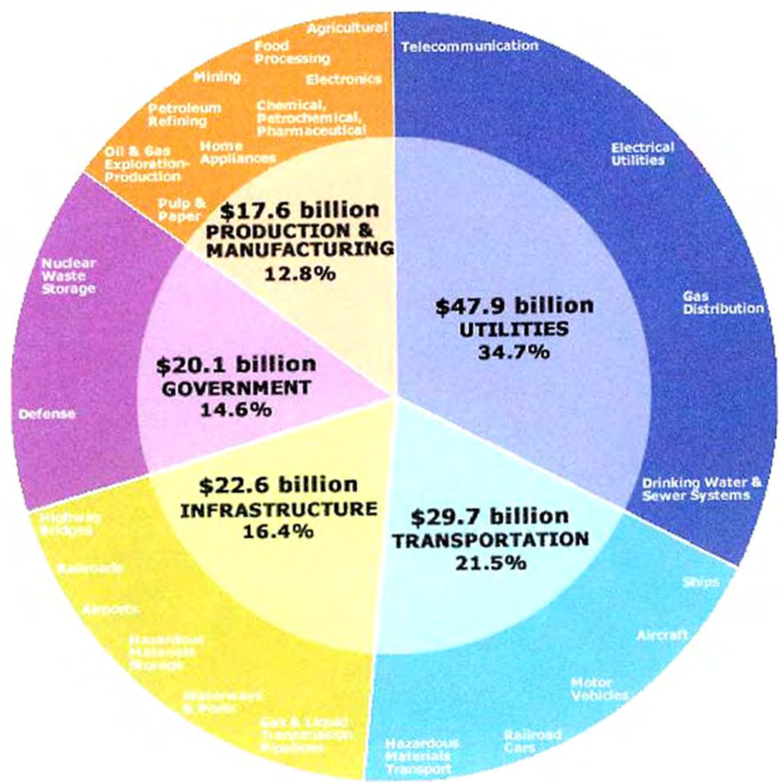
Zin Tun, Mansoor Vezvaie, and the staff at CNBC, Chalk River

Introduction

Corrosion is widespread and expensive

Costs about 3% of GDP in industrialized nations

Report FHWA-RD-01-156

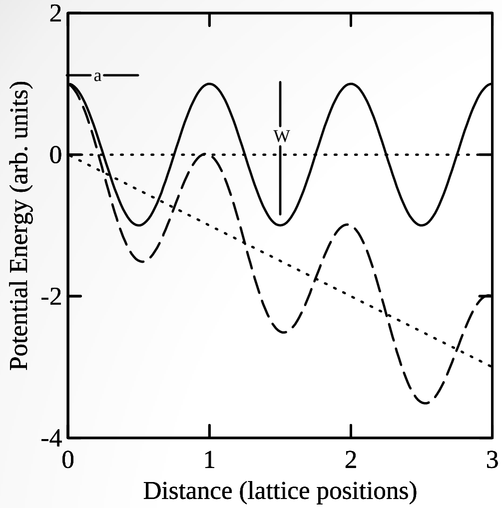


FHWA funds Cost of Corrosion Study.
Total Direct Cost of Corrosion in Analyzed Sectors: $137.9 billion/year (1998).
Extrapolated to U.S. Economy; Cost of Corrosion is $275.7 billion/year (1998).

CORROSION COSTS AND PREVENTIVE STRATEGIES IN THE UNITED STATES. Report by CC Technologies Laboratories, Inc. to Federal Highway Administration (FHWA), Office of Infrastructure Research and Development, Report FHWA-RD-01-156, September 2001.

Neutrons in Corrosion Science

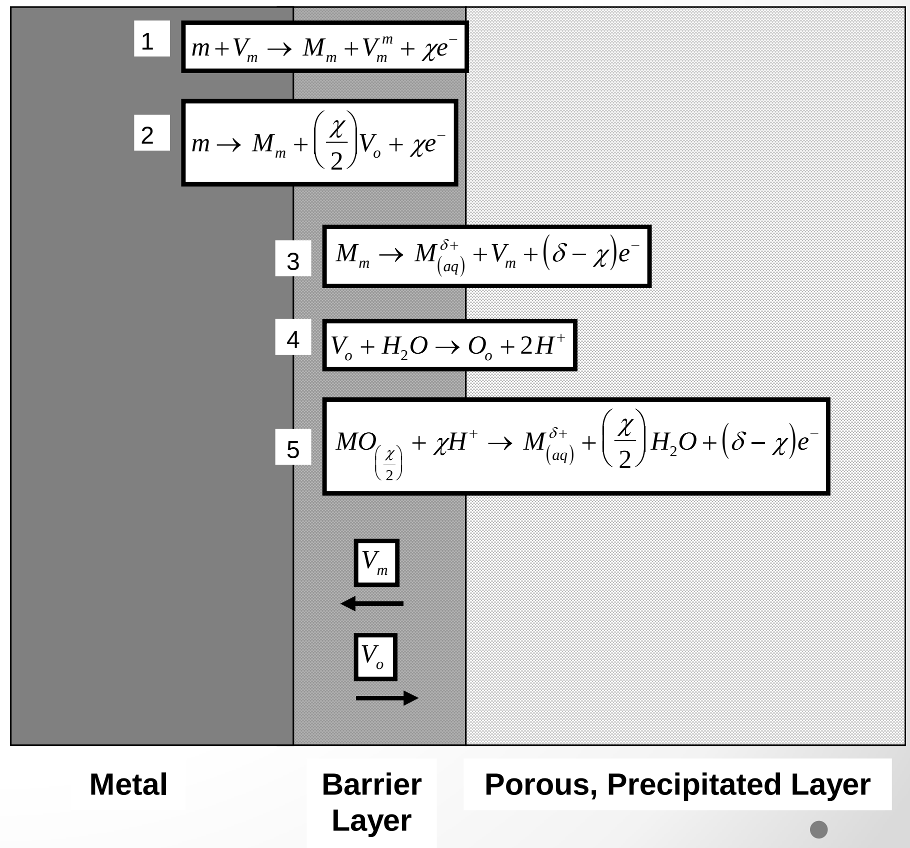
- **Neutron Activation Analysis** (identifying and quantifying corrosion products)
- **Neutron Radiography** (imaging internal features)
- **Small Angle Neutron Scattering: SANS** (investigating particle dispersions, pores)
- **Neutron Diffraction** (measuring strain, crystal structure)
- **Neutron Reflectometry** (probing surfaces, interfaces)
- **Cold Neutron Depth Profiling** (locating certain atoms)



Field-Assisted Ion Transport

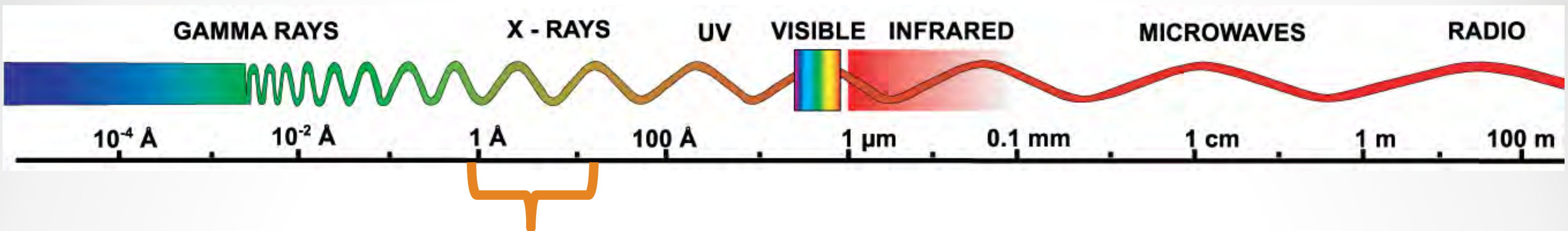
L. Young, "Anodic Oxide Films", Academic Press. London. 1961

The Point Defect Model



D.D. Macdonald, "The point defect model for the passive state", *J. Electrochem. Soc.*, **139**(1992)3434-3449

Use Like X-Rays (almost)

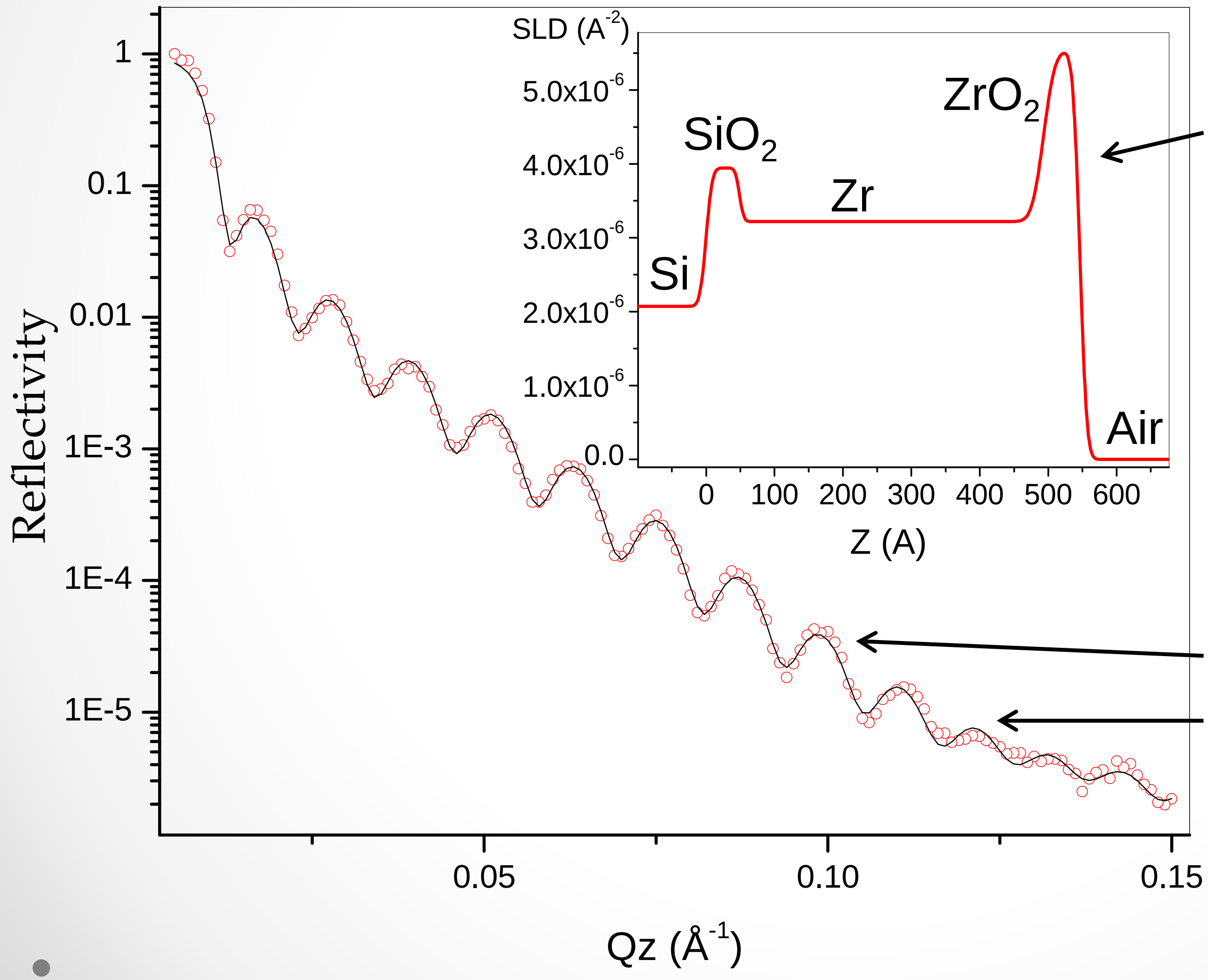


- Both treated with similar principles of "optics"
- Photons interact with electrons (**Z-dependent**), neutrons interact with the nucleus (**<u>not</u> Z-dependent**; e.g., D is very different from H)
- Photon speed 3 x 10^8 m/s, neutrons 2 x 10^3 m/s
- Photon energy eV (visible) to MeV (gamma); Thermal neutron energy meV: **non-destructive**
- Both have a wavelength (λ= h/mv), **refract, diffract, interfere,** can be absorbed, scattered, etc.
-

Nobel Prize 1929 for "for his discovery of the wave nature of electrons."

Zr Film with Native Oxide

As-prepared Zr film in air, neutrons from Si side



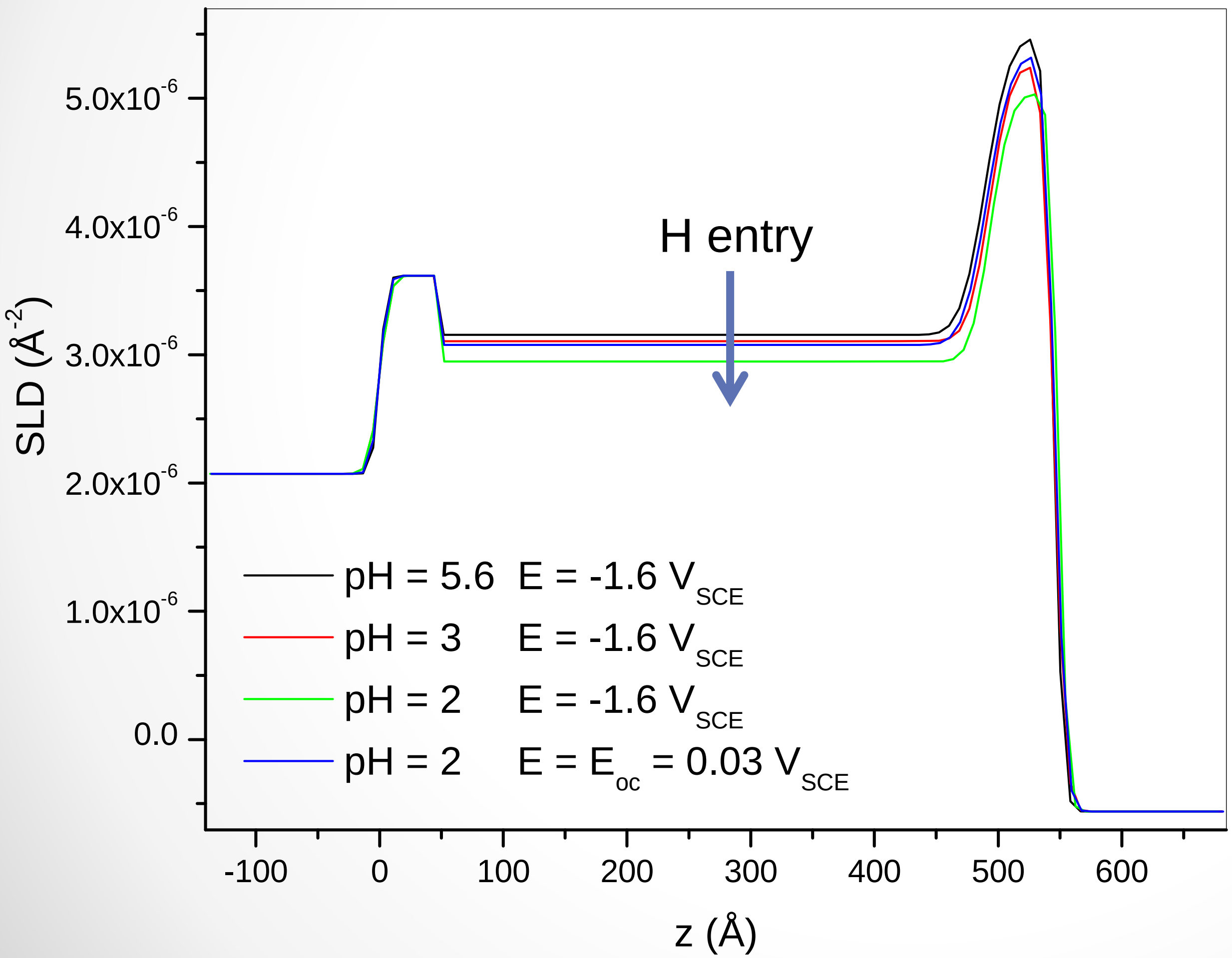
Real Space Profile with layer compositions indicated

Layer	Thickness (Å)
SiO_2	49
Zr	444
ZrO_2	53

Raw Data (red circles)

Fitted Model (black curve)

pH Effect on H Absorption into Zr

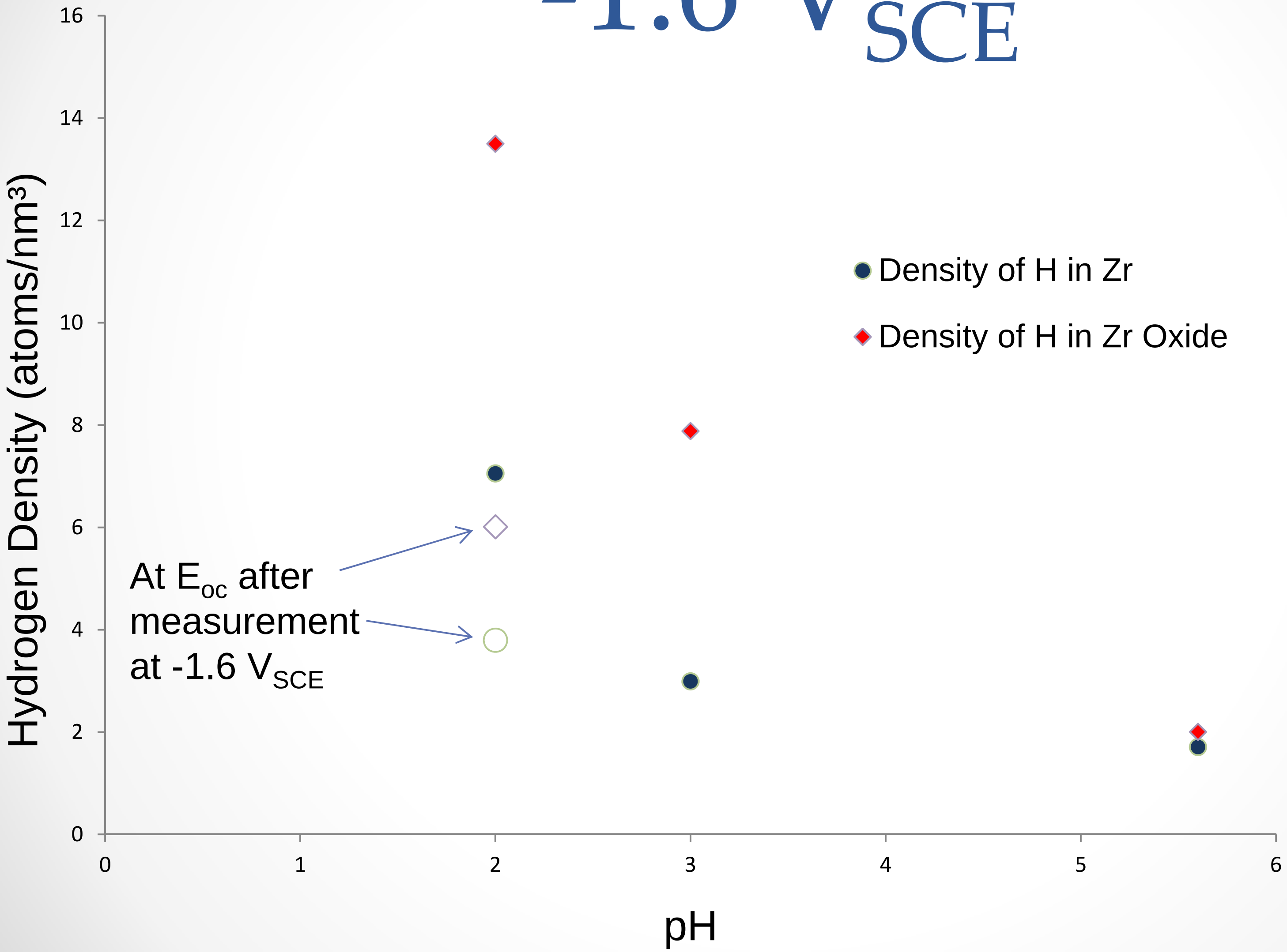


Metal and oxide SLD values decreased as pH decreased under -1.6 V polarization, but rebounded significantly at pH 2 after applied polarization was halted.

Layer thickness values did not change.

Layer	Thickness (Å)
SiO_2	49
Zr	444
ZrO_2	53

H Content of Electrode at -1.6 V_{SCE}



(Note: Metallic Zr has 42.9 Zr atoms/nm^3 and ZrO_2 has 27.8 Zr atoms/nm^3)