High-resolution depth profiling for passive anodized TiO2 ultra-thin films

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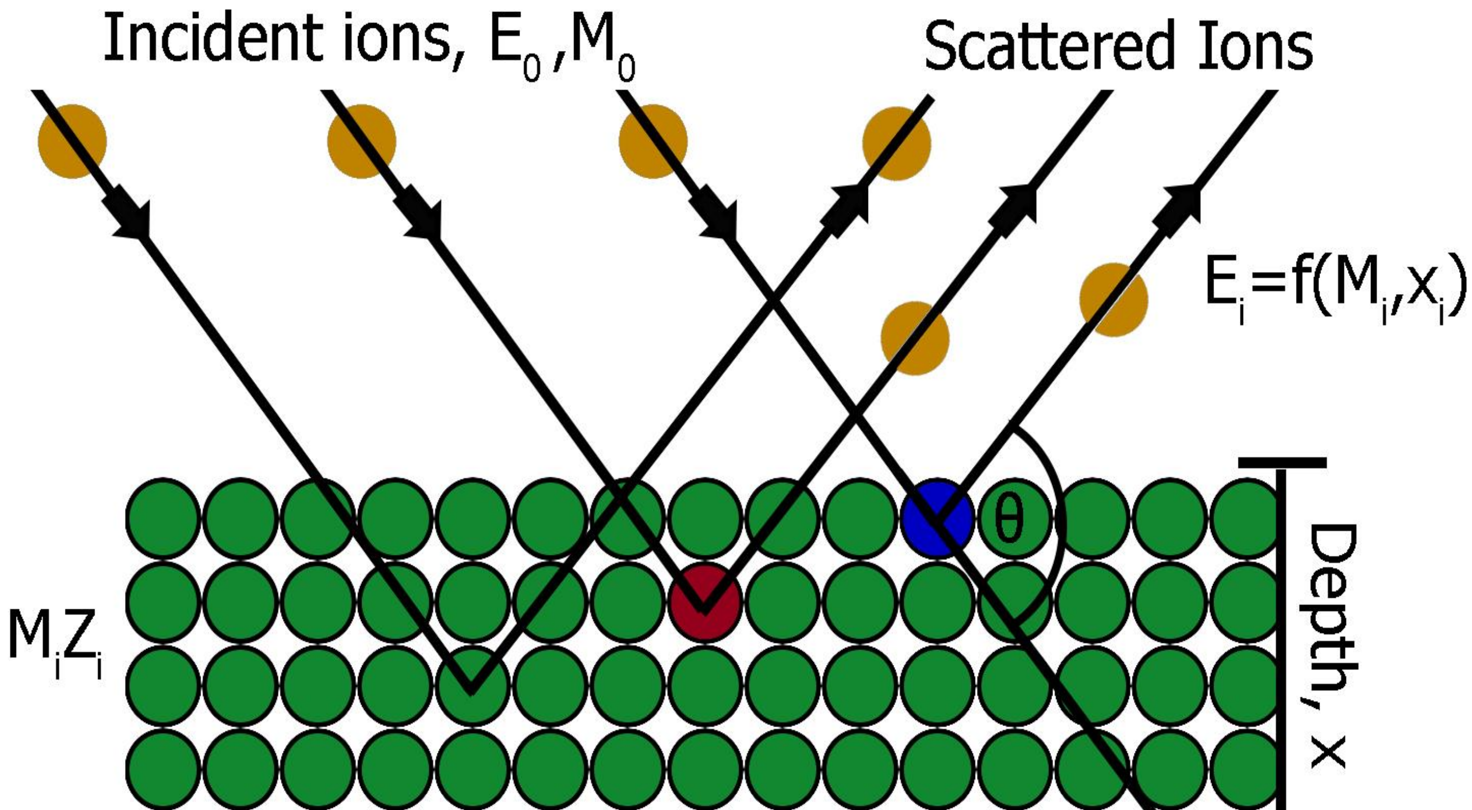
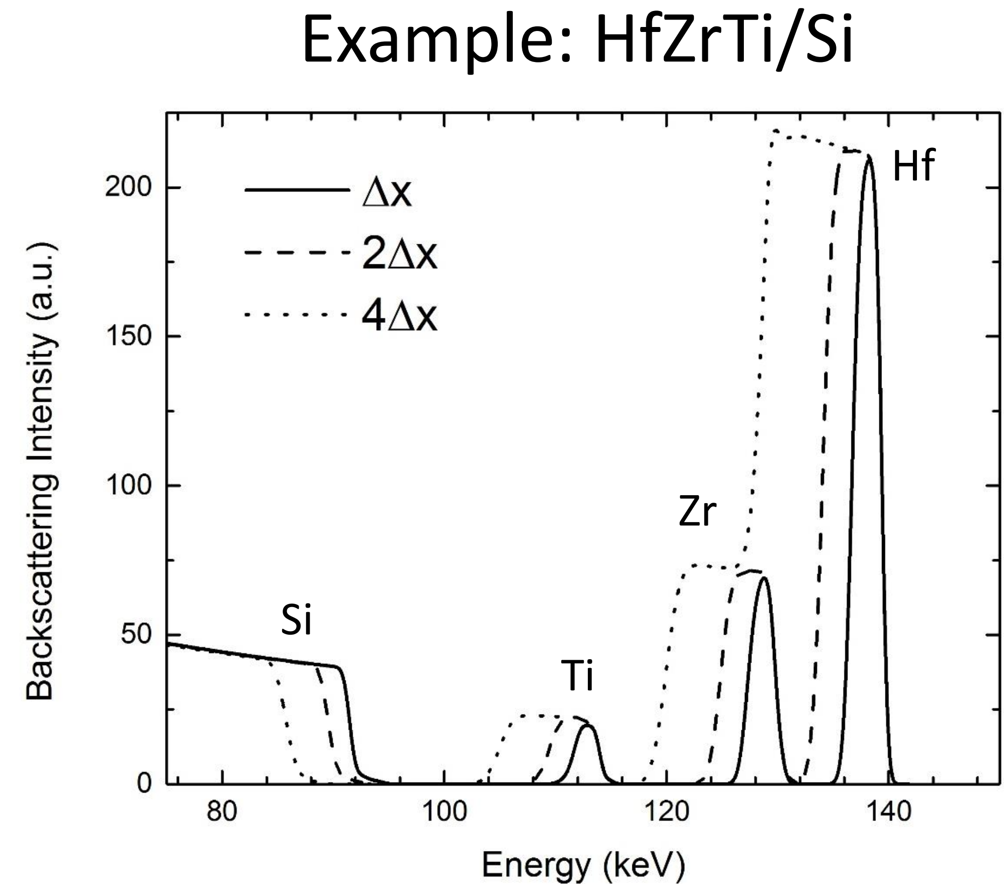
Rutherford Backscattering Spectrometry (RBS)

- A beam of mon-energetic ions bombard a target sample (1-3 MeV)
- The energy distribution of the backscattered ions is analyzed



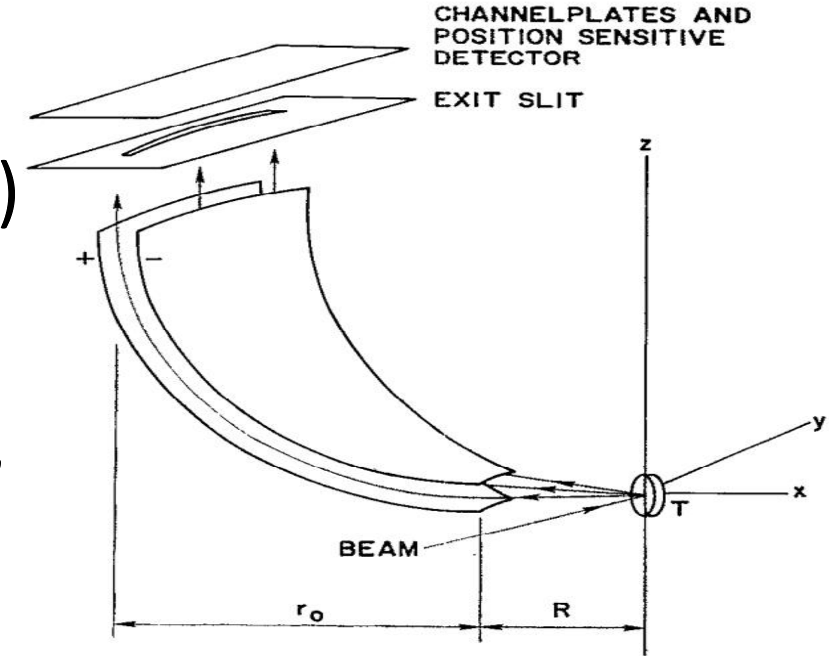
Example: HfZrTi/Si



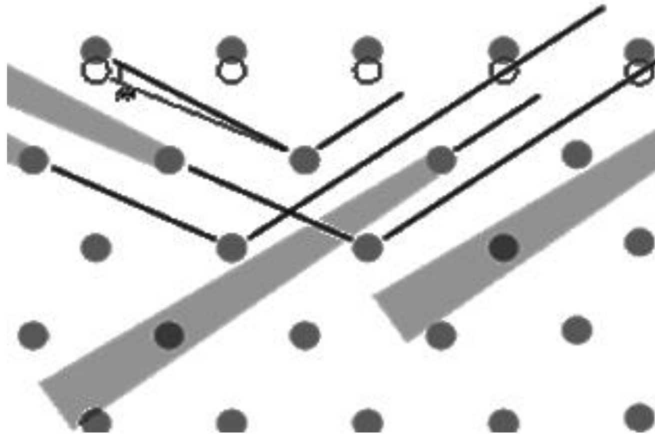
Medium Energy Ion Scattering (MEIS)

Lower incident ions (<200 keV/amu) vs. RBS:

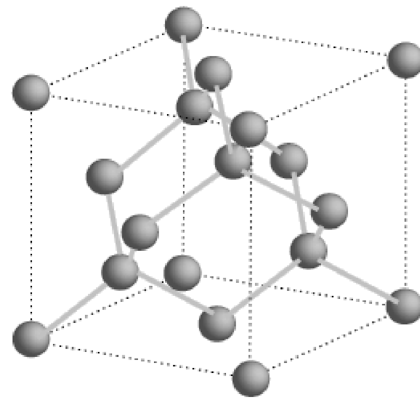
1. Movable toroidal electrostatic analyzer (TEA)
   - High Resolution: $\Delta E/E<10^{-3}$
   - Scattered Ion intensity as a fun. of θ and E_1
2. Channeling & blocking: “Double Alignment”
3. Electronic energy loss maximized for H^+



[1] Tromp et. al. Review of Scientific Instruments 1991, Vol. 62, p2679



Shadowing and blocking: Double Alignment

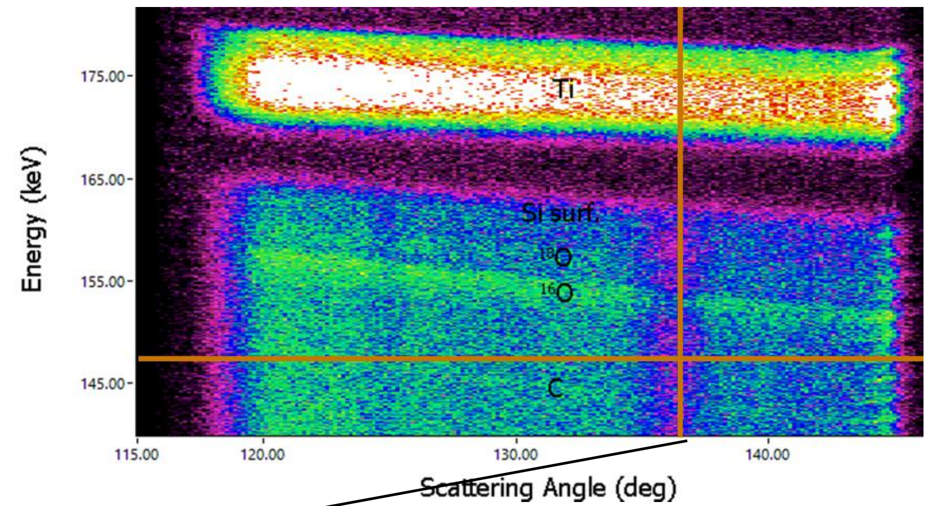


Diamond FFC, Si: 5.4 A

	RBS	MEIS
Ion energy	~ 2 MeV	~ 100 keV
Detector resolution	~ 15 keV	~0.15 keV
Depth resolution	~ 100 Å	~ 3 Å

MEIS Spectrum - TiO_2 Film

- O isotopes resolved, different kinematic factors
- Despite poor low-Z sensitivity
- Channelling and thin film thickness
- MEIS spectra for $TiO_2/Ti/Si(001)$ using 200 keV H^+

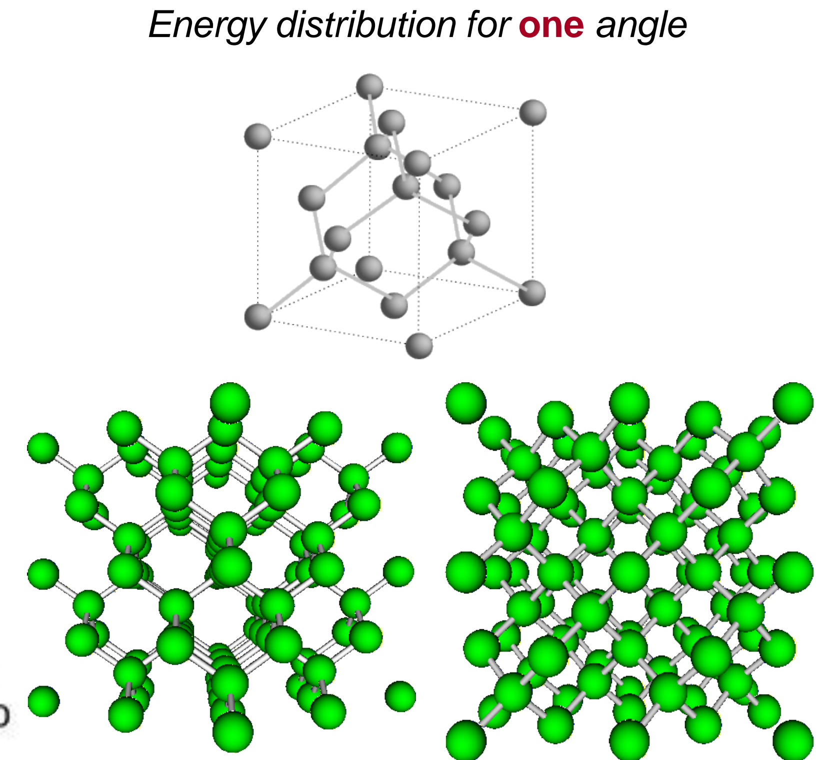


1.5 V $TiO_2/Si(001)$
Incident H^+ energy: 200 kev
Scattering angle: 136.23°

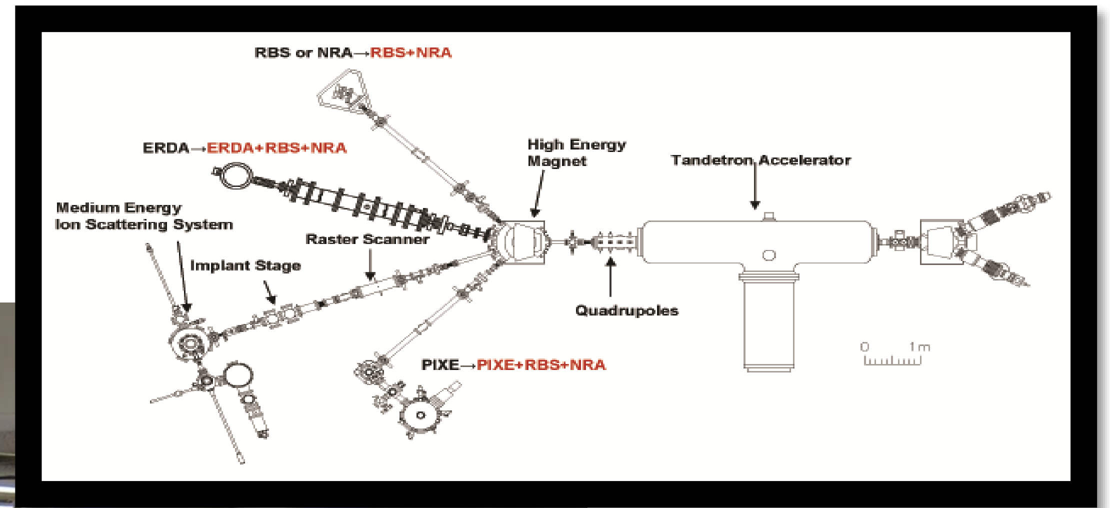
Yeild (a.u.)
250
200
150
100
50
0
C
^{16}O
^{18}O
Si
Ti
140
145
150
155
160
165
170
175
180
Energy (keV)

Carbon contamination: top surface

Energy distribution for ***one*** *angle*



1.7 MeV Tandetron Facility



Beam-lines of Tandetron Accelerator Facility, Western Science Centre G49

Isotopic labeling procedure

- **Ti films deposited** on Si(001) by magnetron sputtering

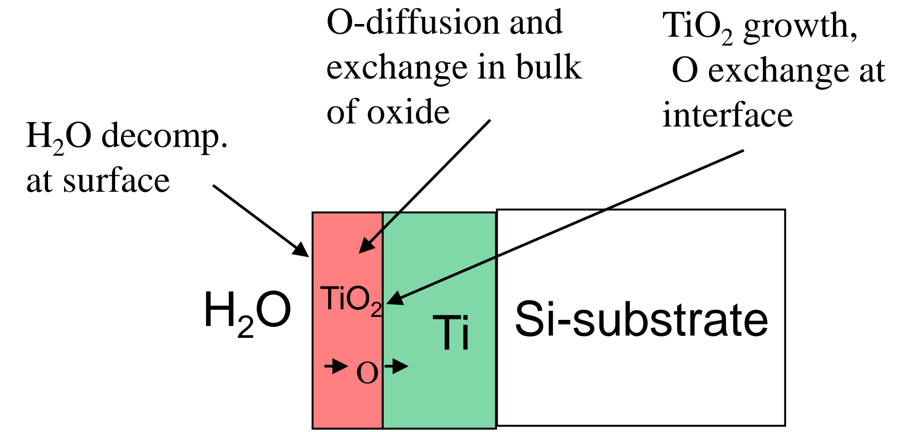
- **“Double oxidation”:**

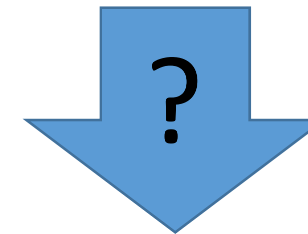
(1)Ti sample is exposed to isotopic (^{18}O) water: ultra thin TiO_2 film ≈10 nm

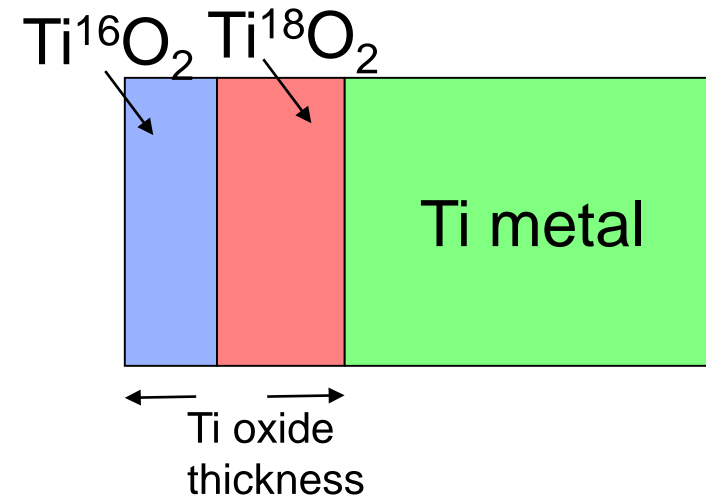
(2)TiO_2/Ti/Si(001) electrochemically oxidized in $H_2{}^{16}O$ water

- **MEIS & NRA**: Depth profiles of elements throughout film

Use depth profiles of O isotopes to infer principles governing oxidation



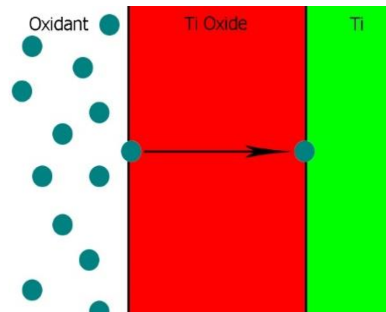


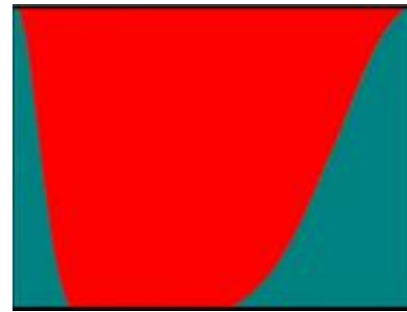


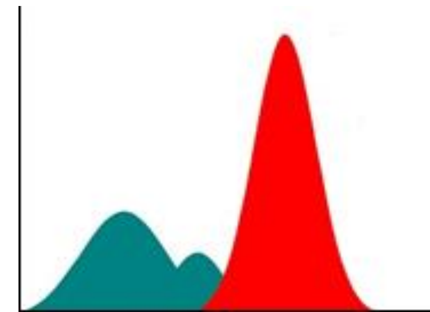
Two major oxygen transport mechanisms

^{18}O ^{16}O

A Interstitial O transport (no exchange) to interface

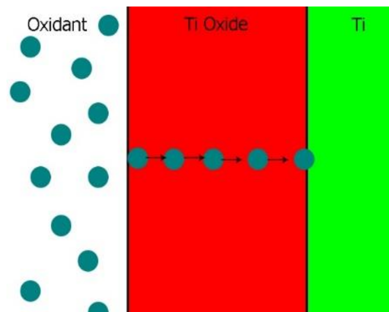


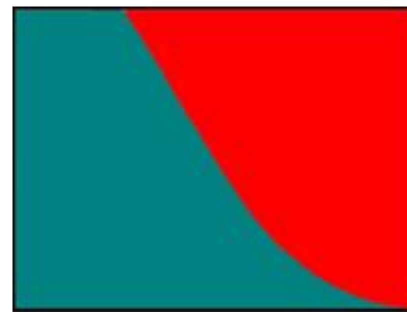




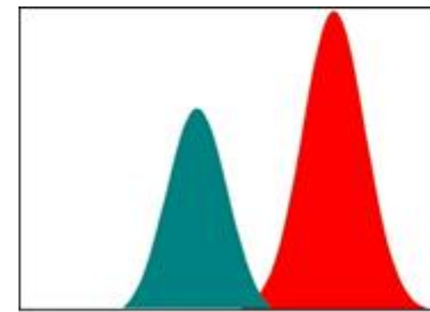
Case A: O is the mobile species and moves interstitially without reacting with the TiO_2 . New oxide forms at the oxide/metal interface

B Oxygen vacancy transport





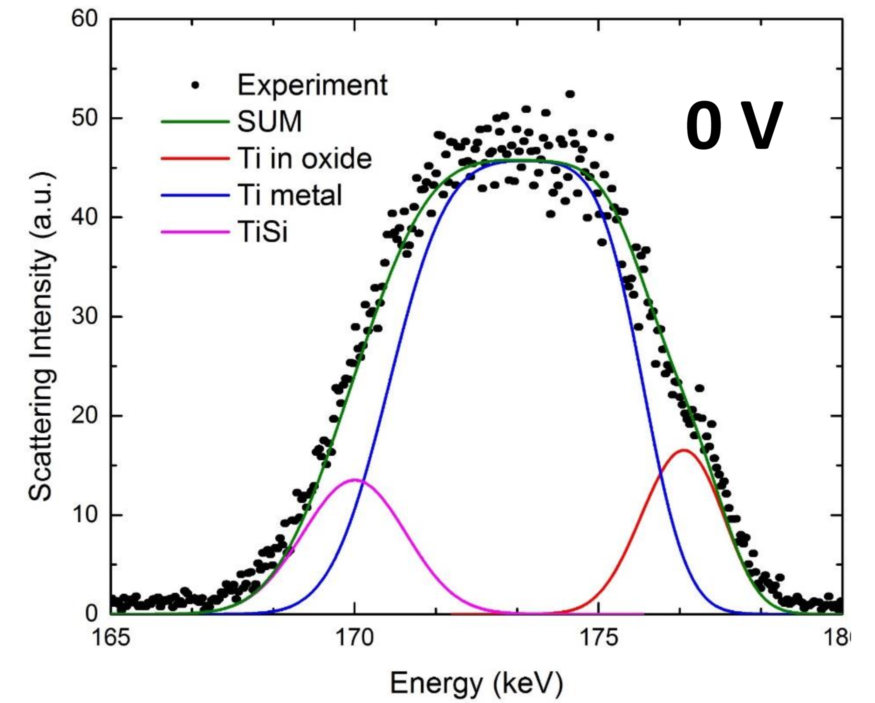
Concentration vs Depth

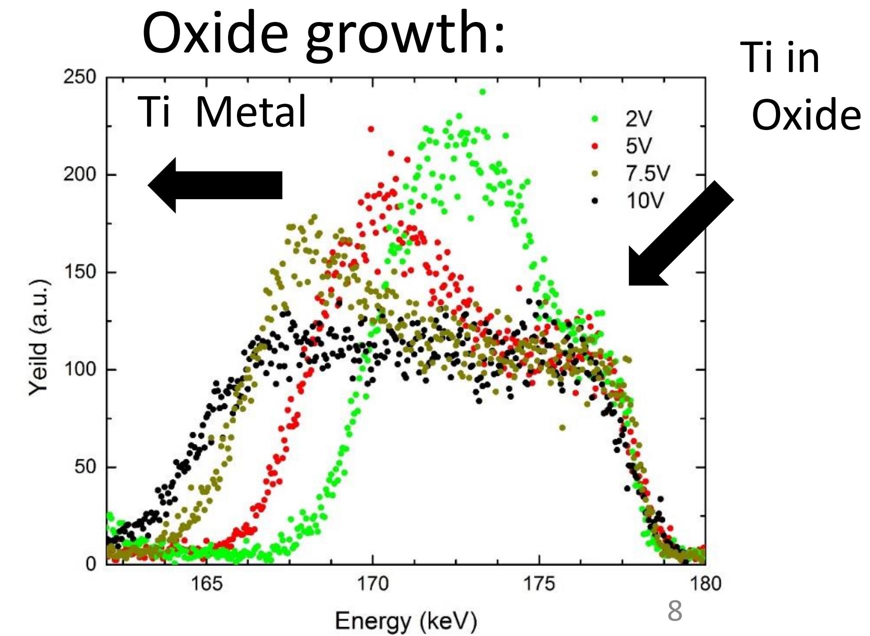


Ion Scattering Yield vs Energy

Case B: If O is the mobile species and there isotopic exchange, results in concentration profile for ^{16}O

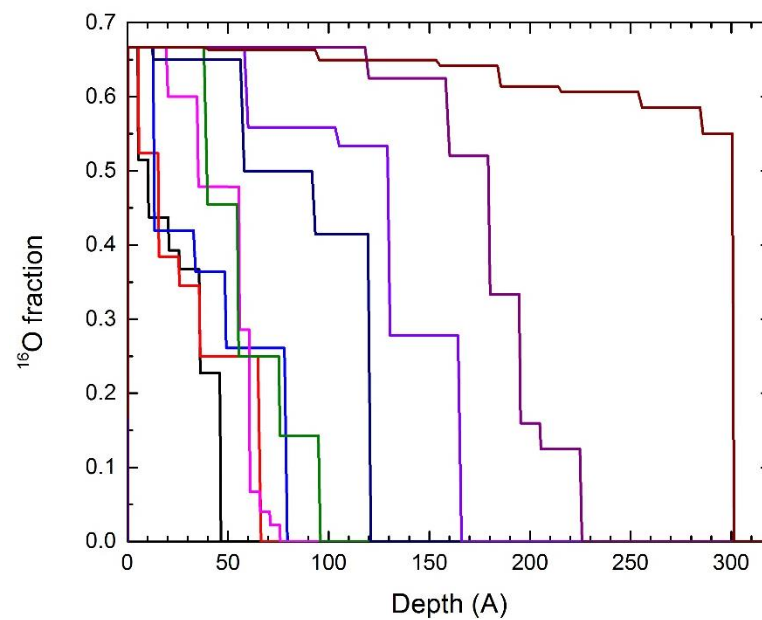
Variation in Ti Features

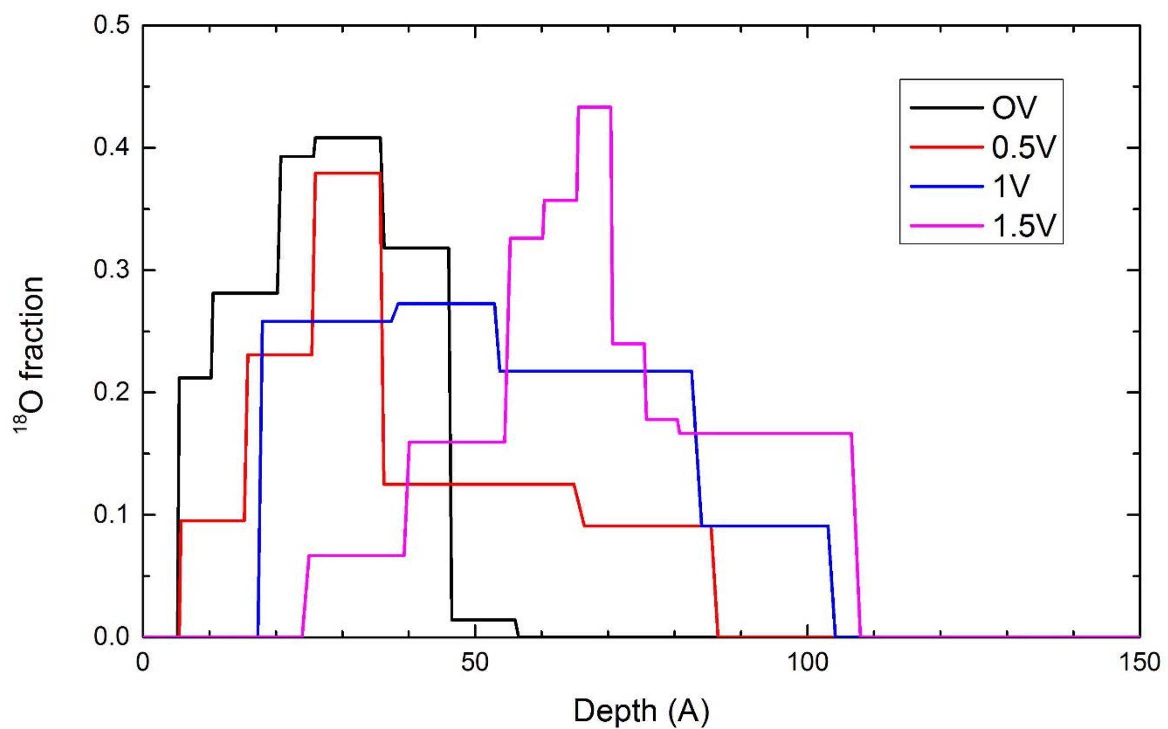


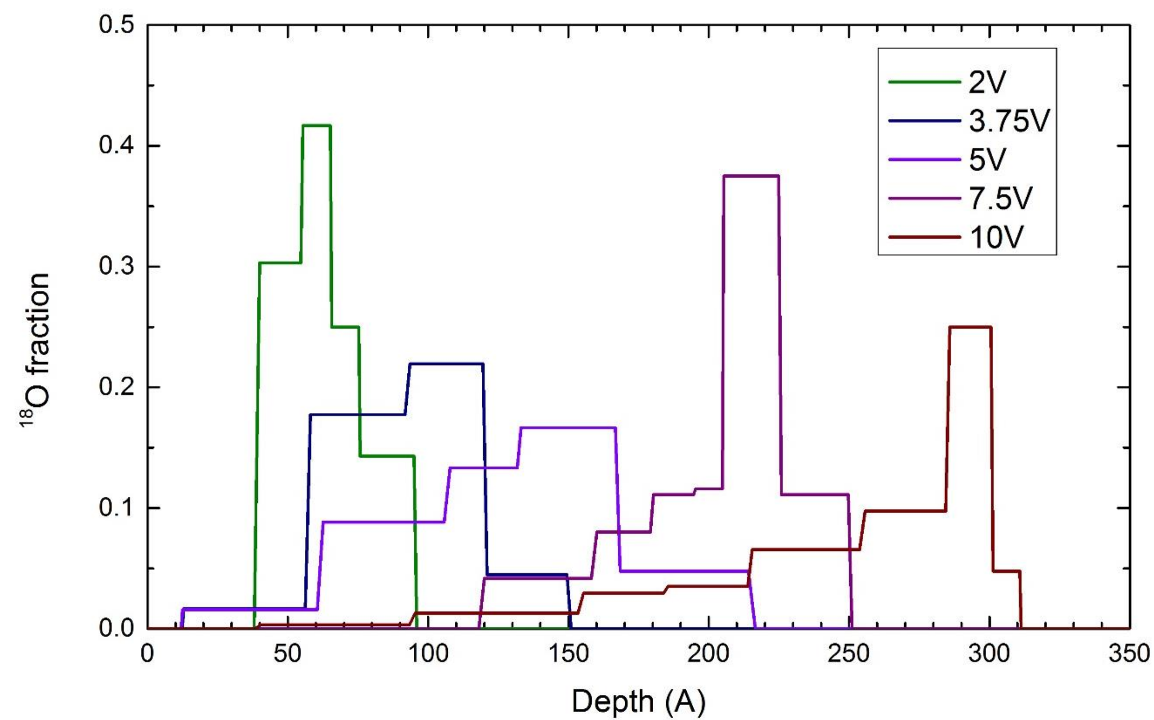


- Experimental Data: Ti and TiO2 as function of voltage
- Oxide growth: not limited to exchange reactions

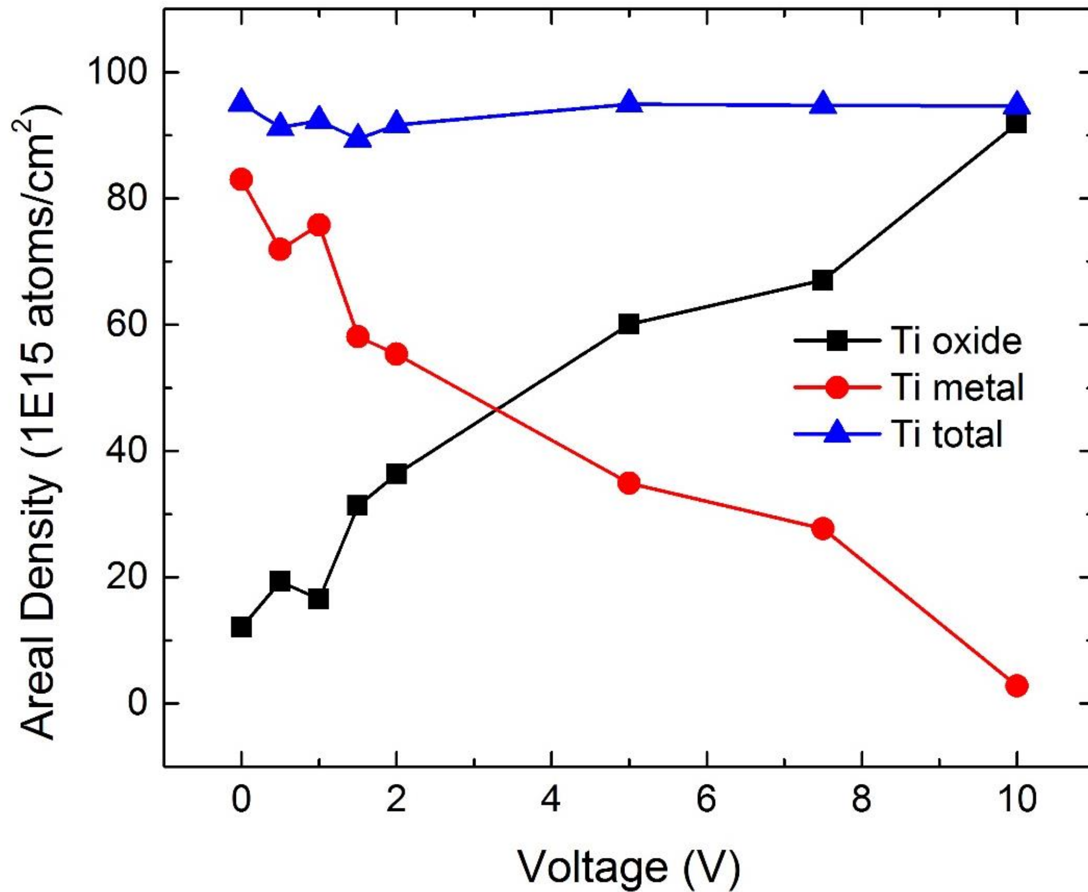
MEIS O depth profiles

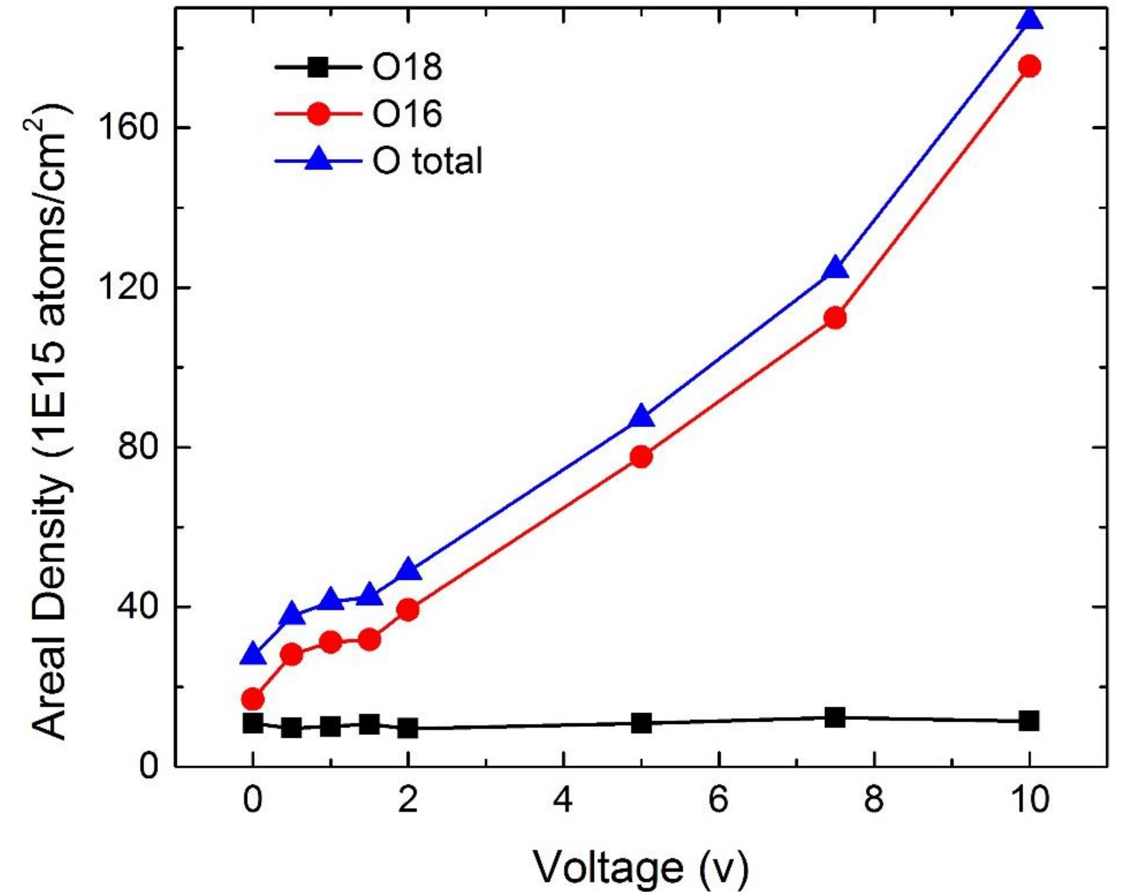






Summary of MEIS



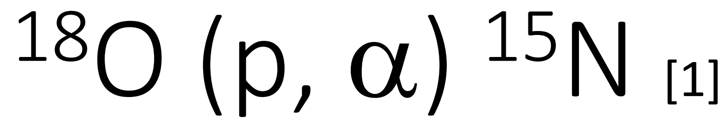


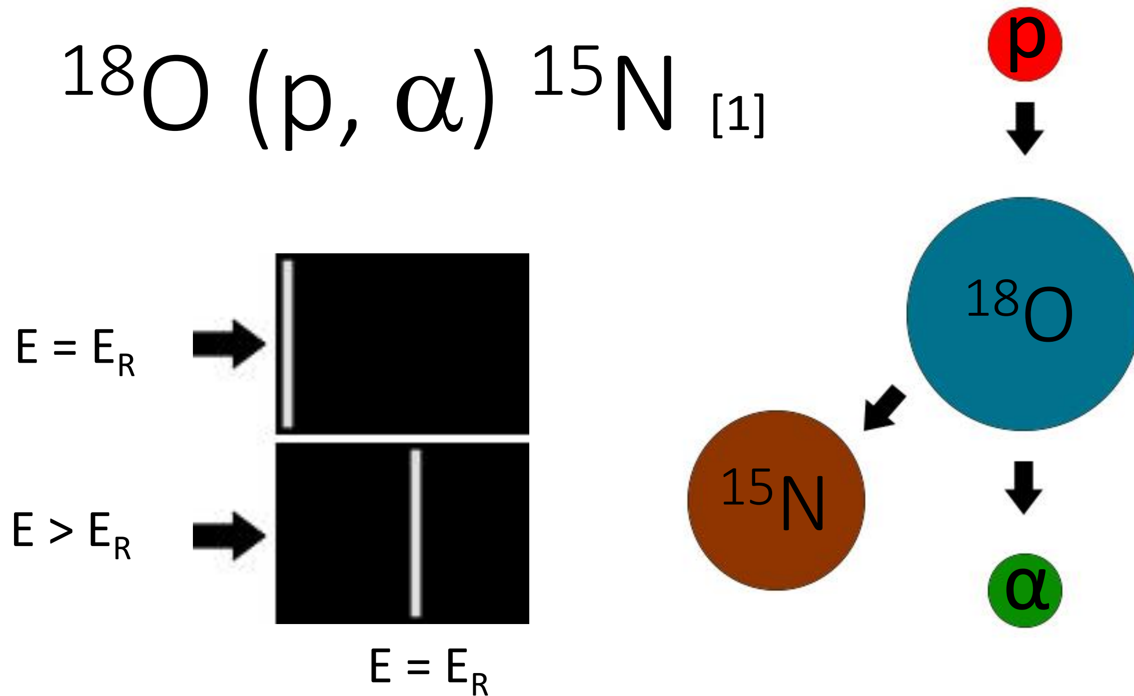
- No Ti lost to liquid phase
- Amount of Ti in oxide form increases as function of voltage
- Commensurately, quantity of Ti metal decreases

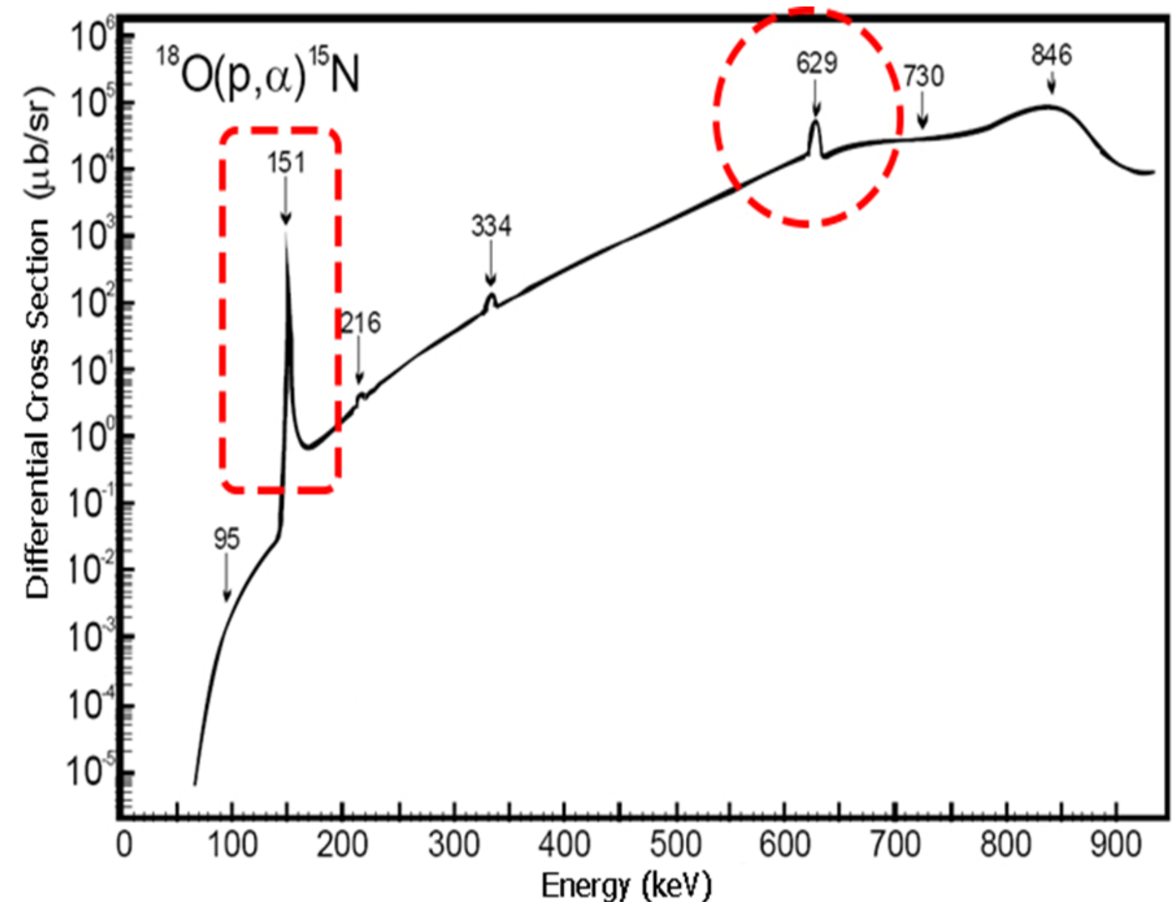
- New Oxide growth from ^{16}O incorporation
- Isotopic exchange at electrolyte/oxide interface
- ^{18}O transport to oxide/metal interface

Nuclear Reaction Analysis (NRA)

Resonance [2]	Width	Depth Resolution
151	0.05	High
629	2.1	Low



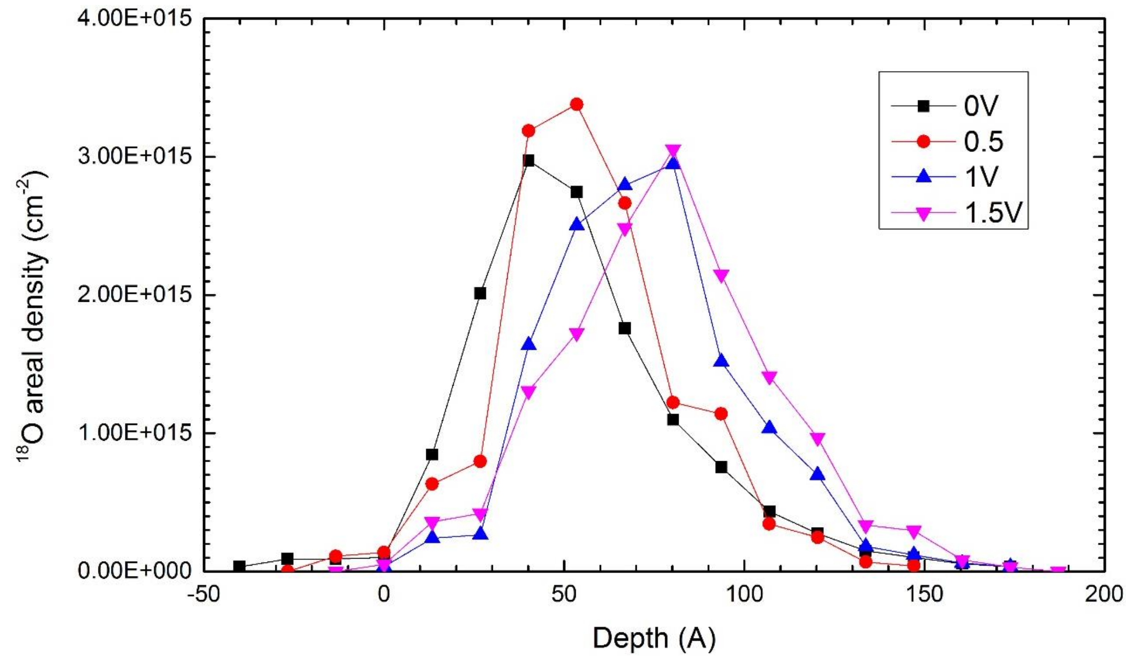


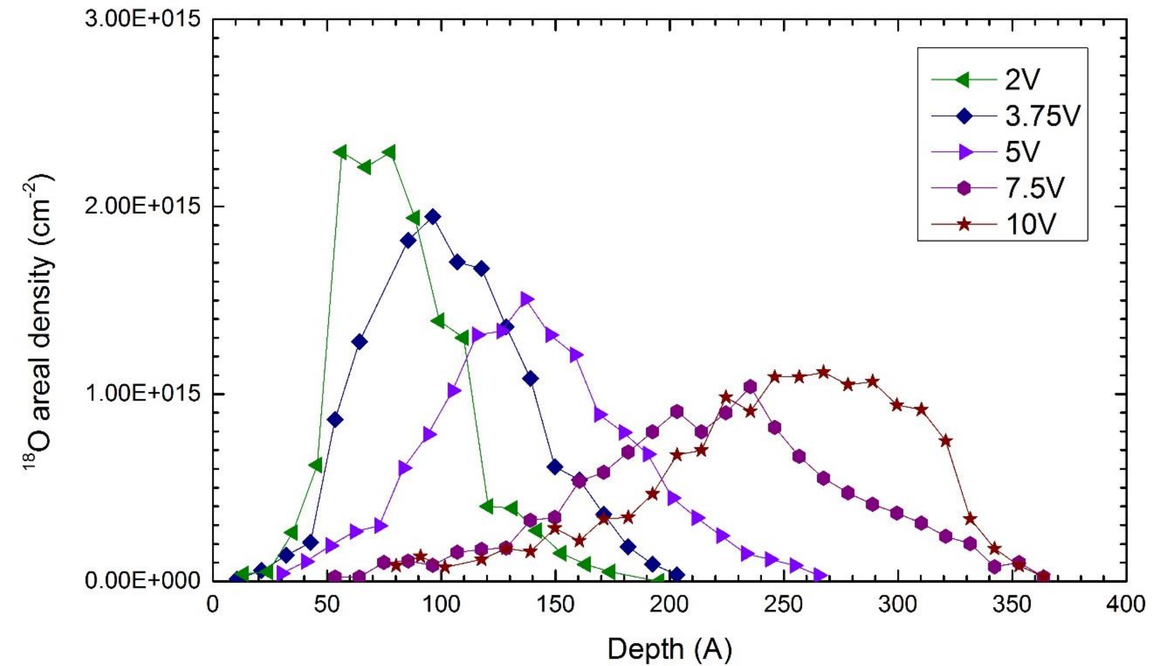


[1] Baumvol. *Surface Science Reports* 36 (1999), [2] Battistig et al. *Nuclear Instruments and Methods B 61 (1991)*

NRA O depth profiles

- Convert alpha intensity to areal density with standard
- Depth scale determine by energy loss (stopping power) of protons in the medium

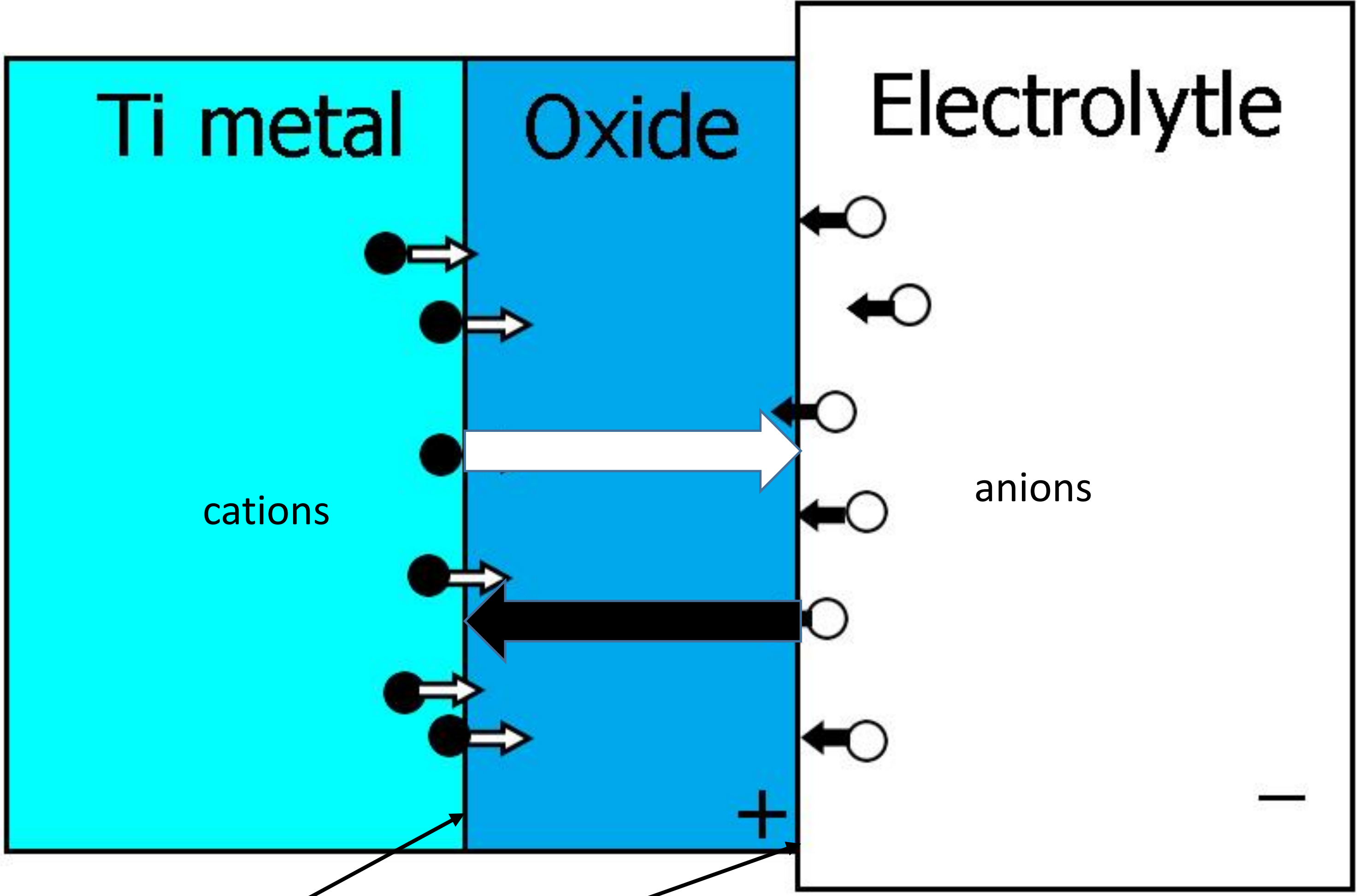




Two major modeling approaches: “high-field” model [1]

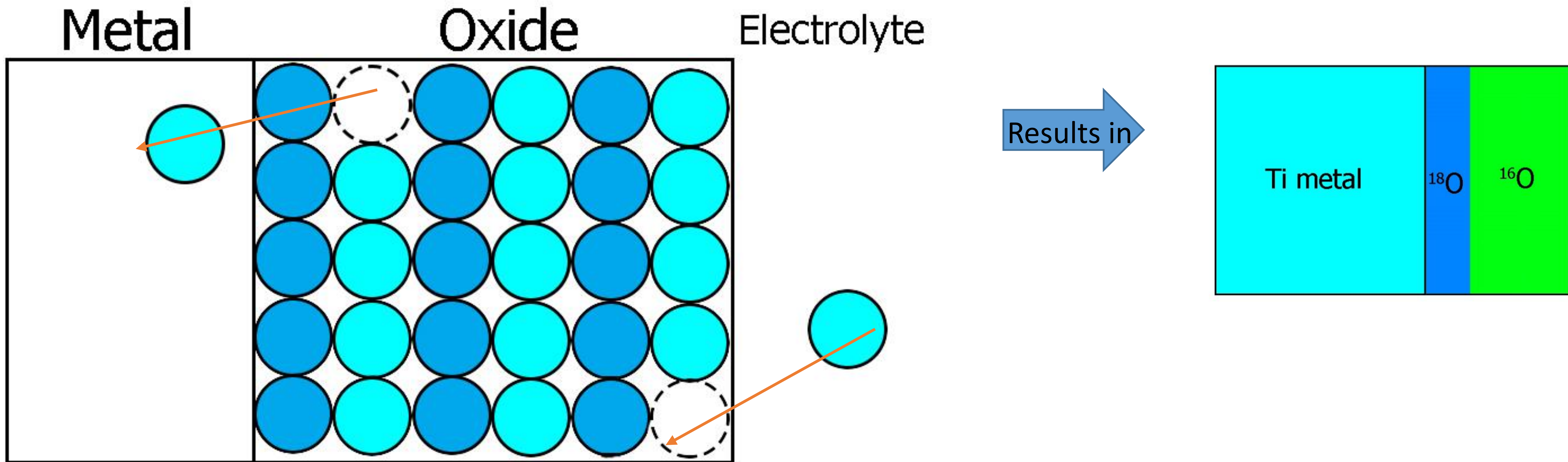
- Driven by electric field in oxide, about 4E8 V/m [2]
- Both cations and anions have mobility
- Ion transport: just migration
- Diffusion is negligible

$$i_c = i_o \exp(\beta \cdot E) \quad (1)$$



[1] L. Young, Anodic Oxide Films, Academic Press, London (1961). [2] Z. Tun et al., J. Electrochem. Soc. 146, 988 (1999), [3] N. Khalil and J.S.L. Leach, Electrochim. Acta 31, 1279–1285 (1986).

“low-field”: point-defect model (PDM) [3]



- Classical Fick and Nernst-Einstein equations are used to describe transport of ions

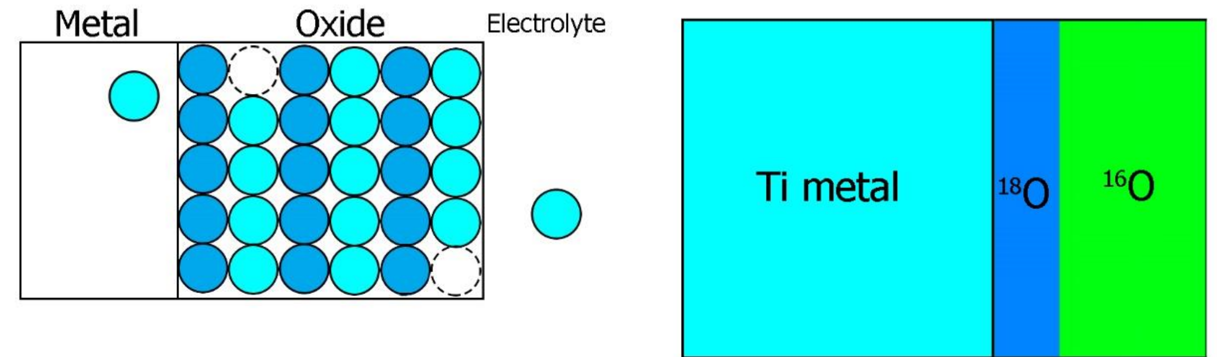
$$i_c = -zFD_c \frac{dc_c}{dx} - zF\mu c_c \frac{d\phi}{dx}$$

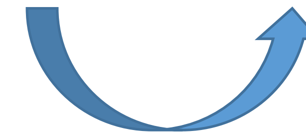
- Shielding effects at surface: low E through oxide
- Transport: migration & diffusion!

[3] D. D. Macdonald, J. Electrochem. Soc., 139, 3434 (1992).

Conclusions

- Oxide growth increases as function of voltage
- New oxide created by ^{18}O diffusing towards the oxide/metal interface
- Increasing incorporation of ^{16}O towards electrolyte/Oxide interface: O exchange
- Depth profiles consistent with the Point defect model
- Proceeds by vacancy mechanism, separately on the O and Ti sublattices due to strong ionic chemical bond between constituents





Results in

Thank you!

I want to thank

- Lyudmila Goncharova, my supervisor
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- Jack Hendriks for Tandetron operation

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