High Resolution Depth Profiling of Ti Oxidation

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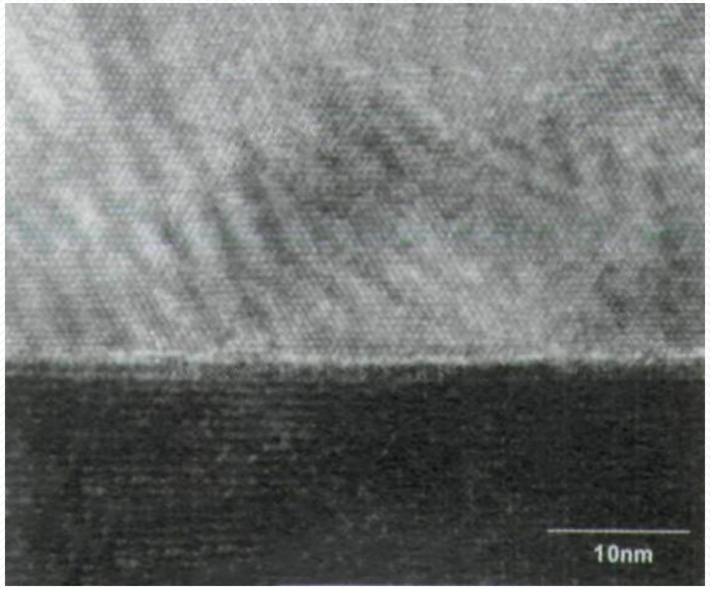
Motivations

- Ti is widely used in industry and research
- Oxidation processes:
  - -Thermal: lack of precise control → > 100 nm
  - -Electrochemical (time vs voltage): high quality ultra-thin films (≈10 nm)

- Corrosion specific to Ti
- General principles of electrochemical oxidation:
  - -Dominant migrating species
  - -Exchange reactions
  - -Transport mechanisms

- Stopping power for H^+ in Ti and TiO_2 ultra-thin films



Matsumoto et. al. Science, 2001. Vol. 291, p854-856

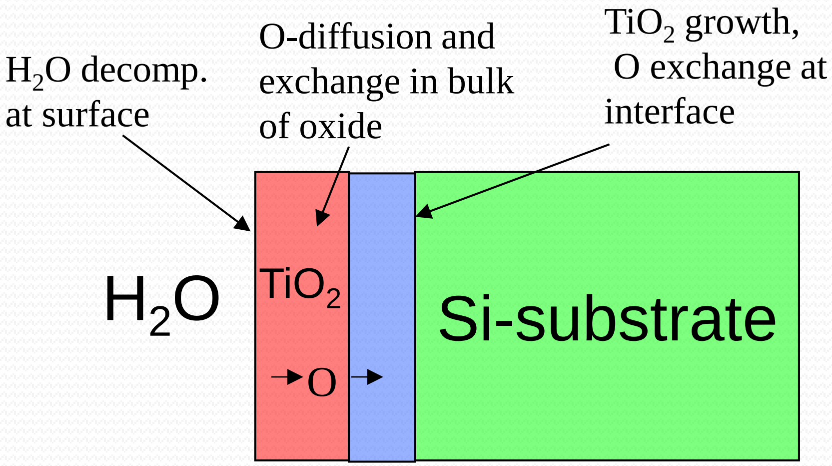
Procedure

- **Ti films deposition** on Si(001) by sputtering (with J. Noel, Chemistry, UWO)

- **Isotopic labeling:**
  - Ti sample is exposed to isotopic (^{18}O) water
    - Ultra thin TiO_2 Film
  - TiO_2/Ti/Si(001) electrochemically oxidized in $H_2{}^{16}O$ water

- **Medium Energy Ion Scattering** (MEIS):
  - Analyze surface layers at sub-nanometer depths
  - Simulation of depth profiles of isotopes

- **Other analytic techniques:**
  - X-ray Photoelectron Spectroscopy (XPS): Ti oxidation state
  - Nuclear Reaction Analysis (NRA): Absolute ^{18}O conc., potential depth profiling



H_2O decomp. at surface

O-diffusion and exchange in bulk of oxide

TiO_2 growth, O exchange at interface

H_2O

TiO_2

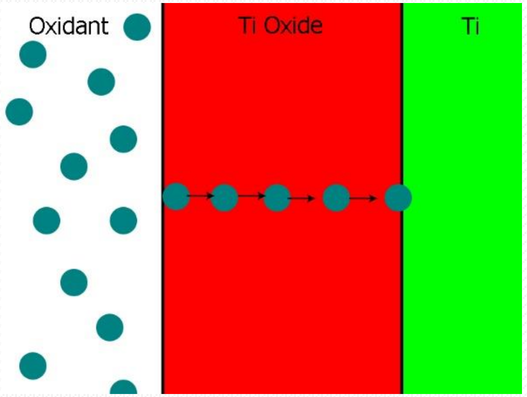
→O →

Si-substrate

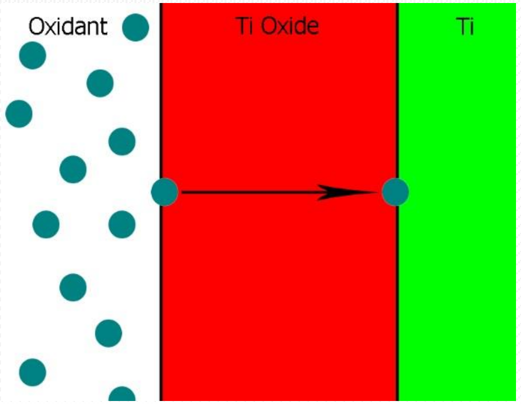
Two Major Oxygen Transport Mechanisms

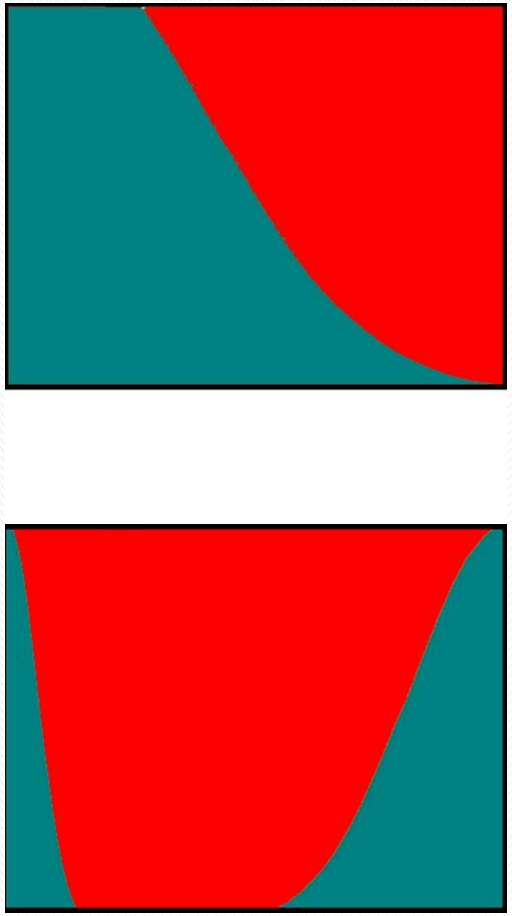
🟥 ^{18}O ■ ^{16}O

Oxygen lattice transport (O or vacancy exchange)

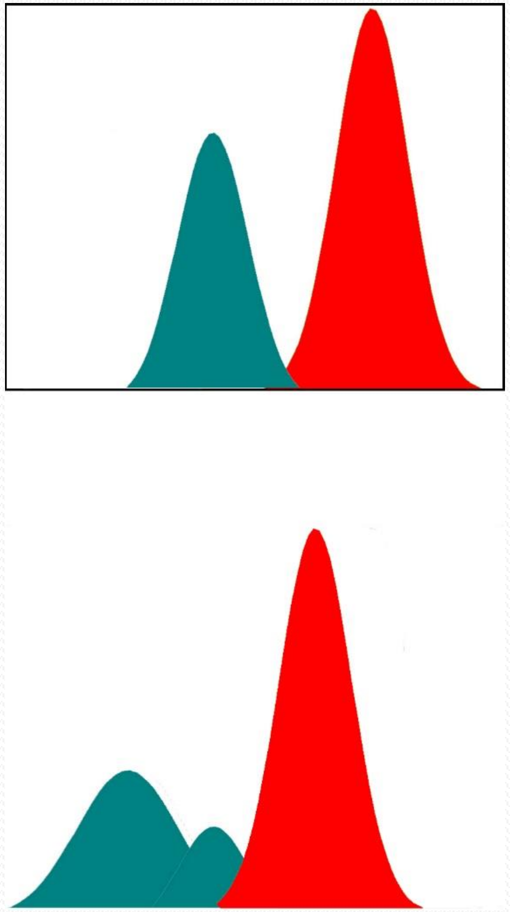


Direct oxygen transport (no O-exchange) to interface



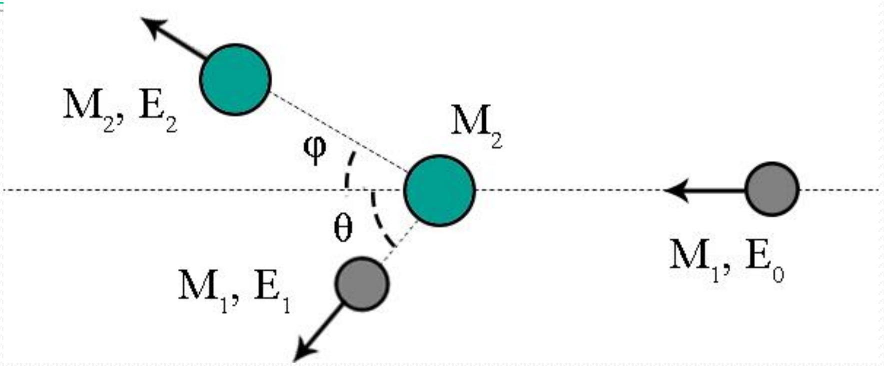


Concentration vs Depth



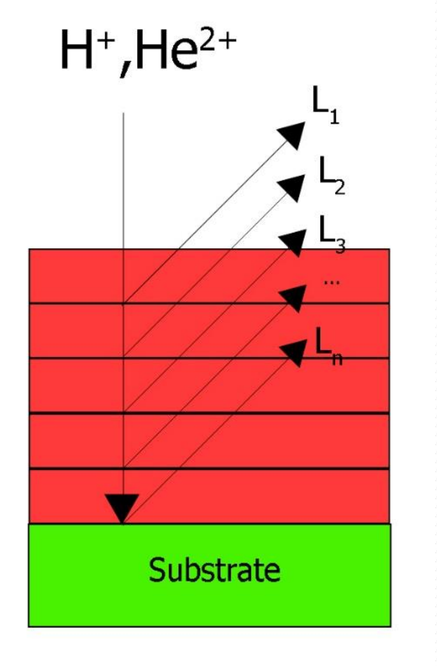
Ion Scattering Yield vs Energy

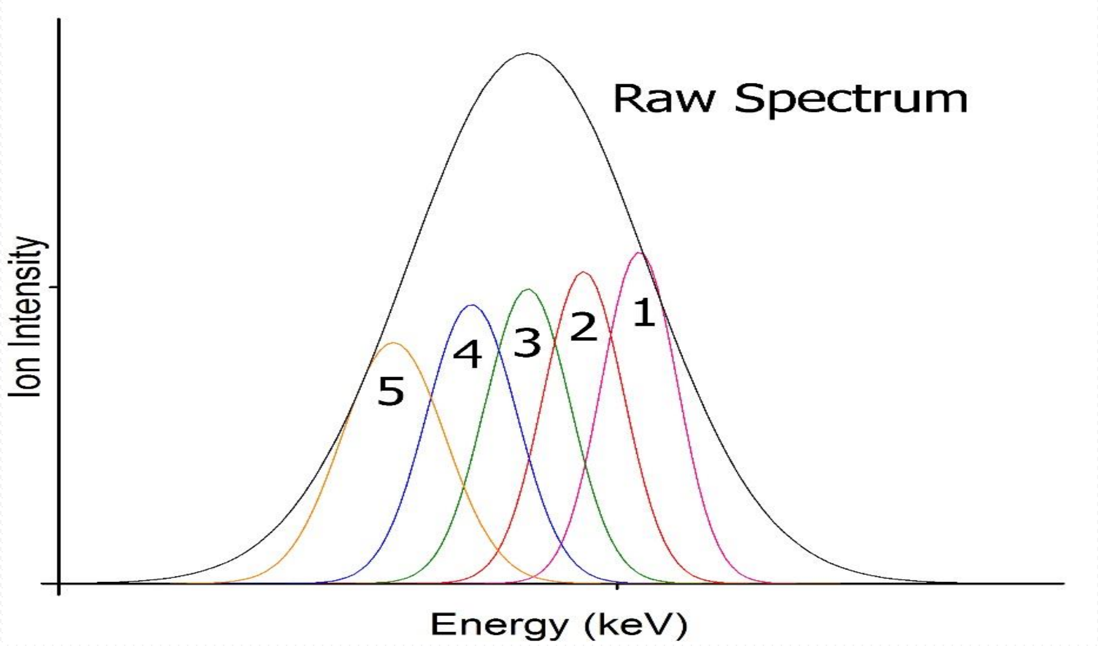
Rutherford Backscattering Spectrometry (RBS) and Depth Profiles



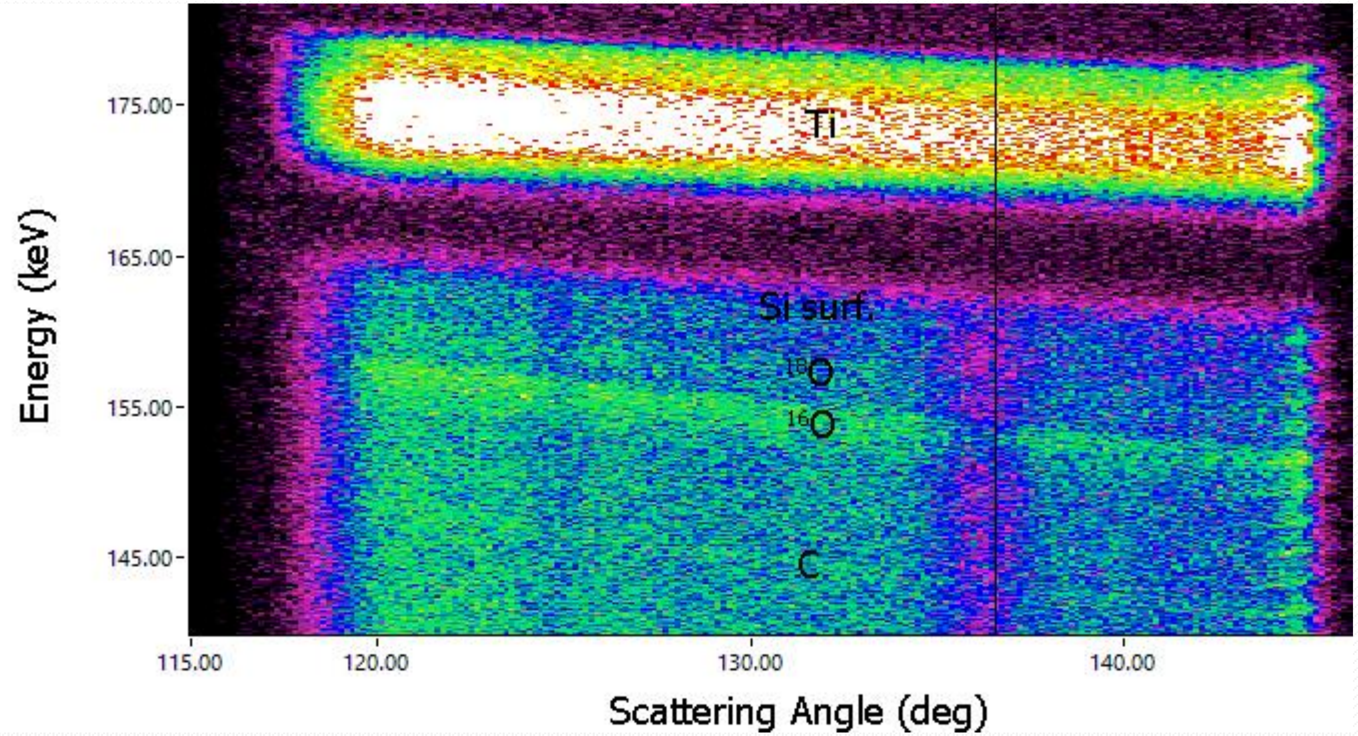
- Incident beam of mono-energetic ions
- Scattered off target → element/isotope sensitive
- Know M_1, E_o and θ (detector placement)
- Measure E_1 → determine M_2

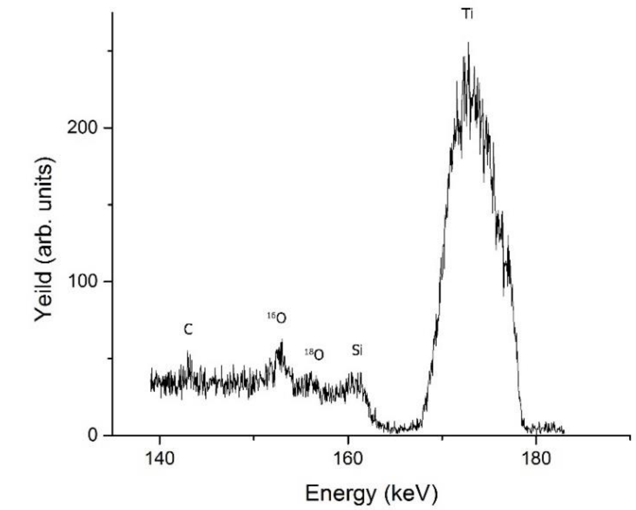
$$K = \frac{E_1}{E_o} = \left[\frac{(M_2^2 - M_1^2 \sin^2\theta)^{1/2} + M_1 \cos\theta}{M_1 + M_2}\right]^2$$

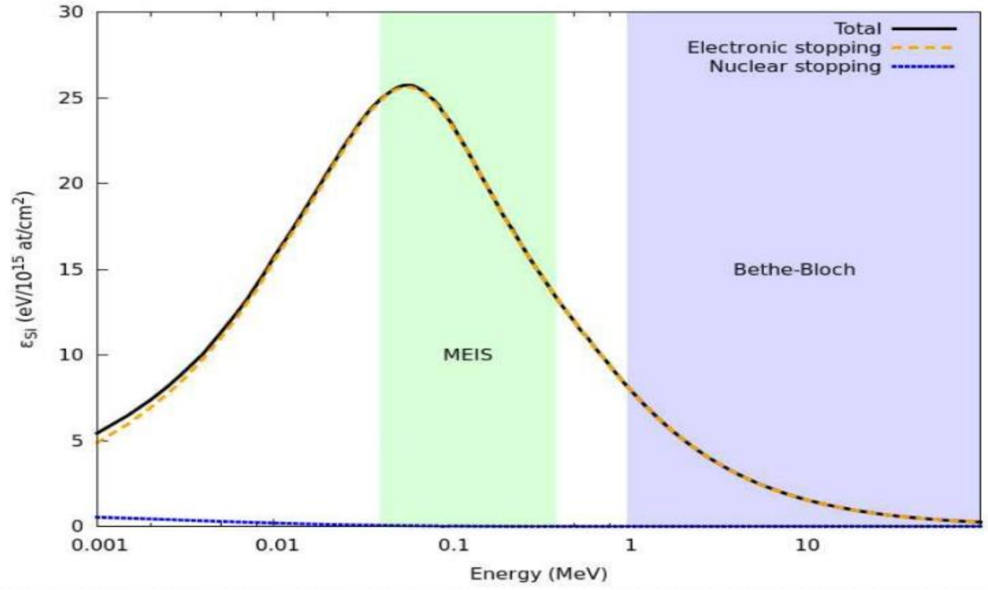




Medium Energy Ion Scattering (MEIS)





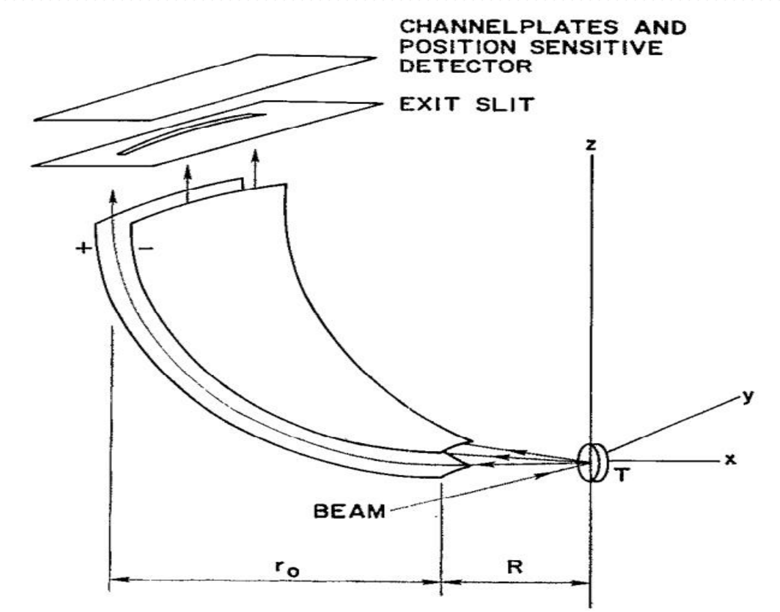


Identical to RBS, but:

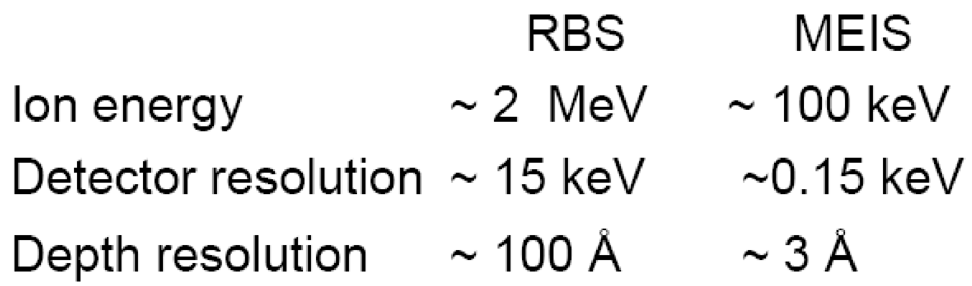
- Torrodial Electrostatic Analyizer (TEA):
  - -Scattered Ion intensity as a function of scattering angle, at fixed energy
- Channeling incident beam and movable detector positioned to blocking direction: “Double Alignment”

PSTAR database (NIST): http://www.nist.gov/pml/data/star/index.cfm

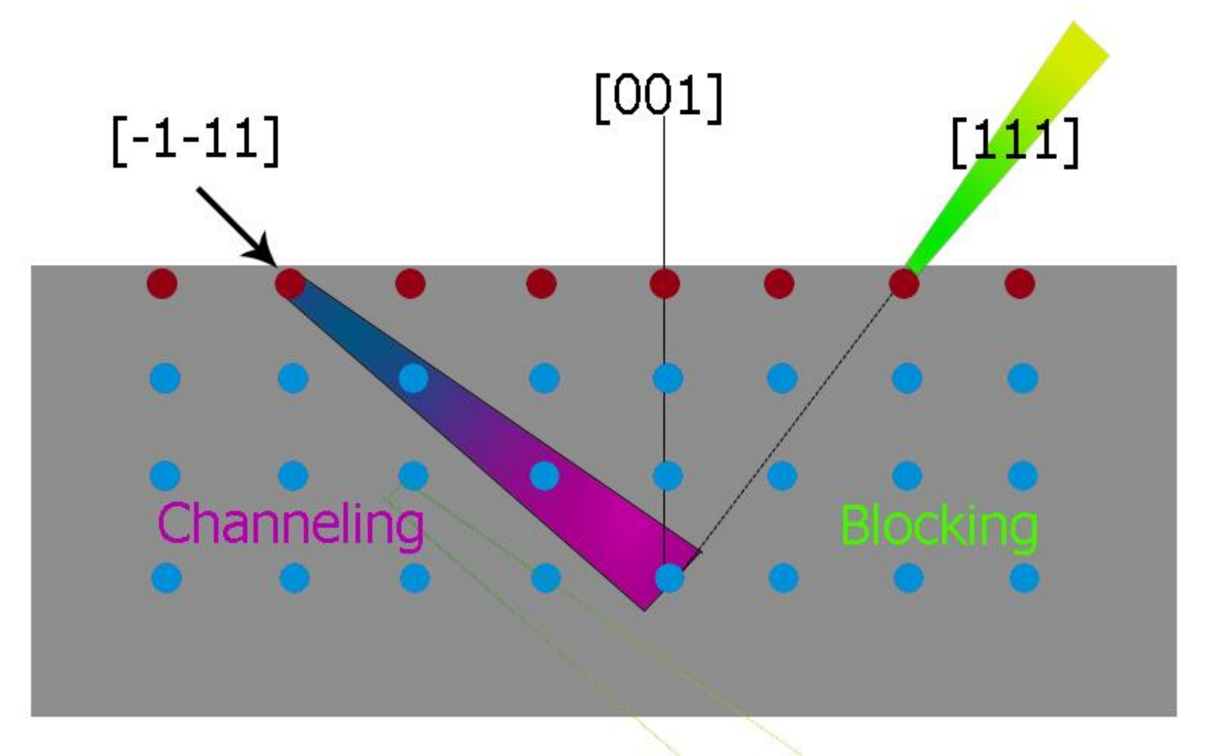
TEA and Double Alignment



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

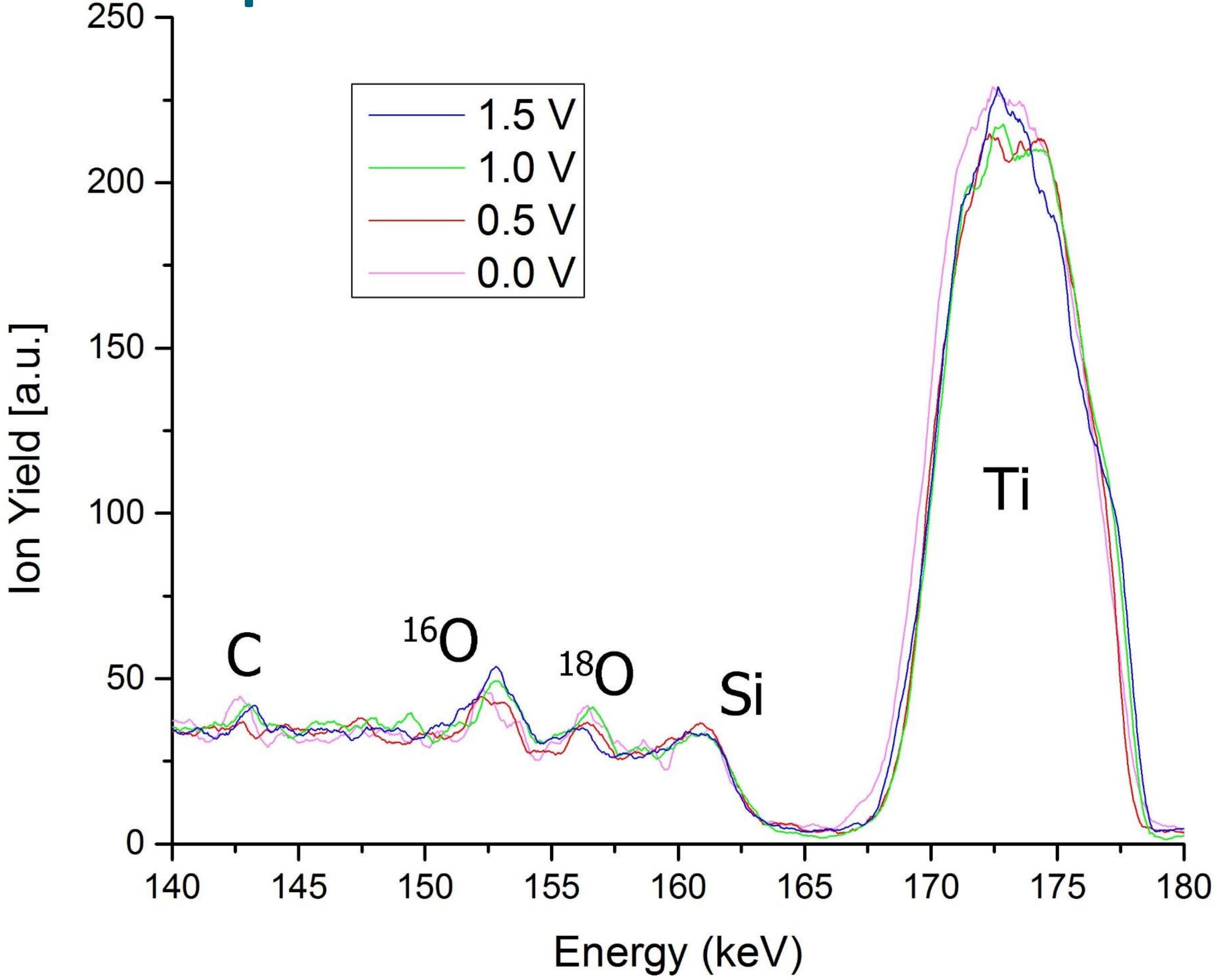


	RBS	MEIS
Ion energy	~ 2 MeV	~ 100 keV
Detector resolution	~ 15 keV	~0.15 keV
Depth resolution	~ 100 Å	~ 3 Å

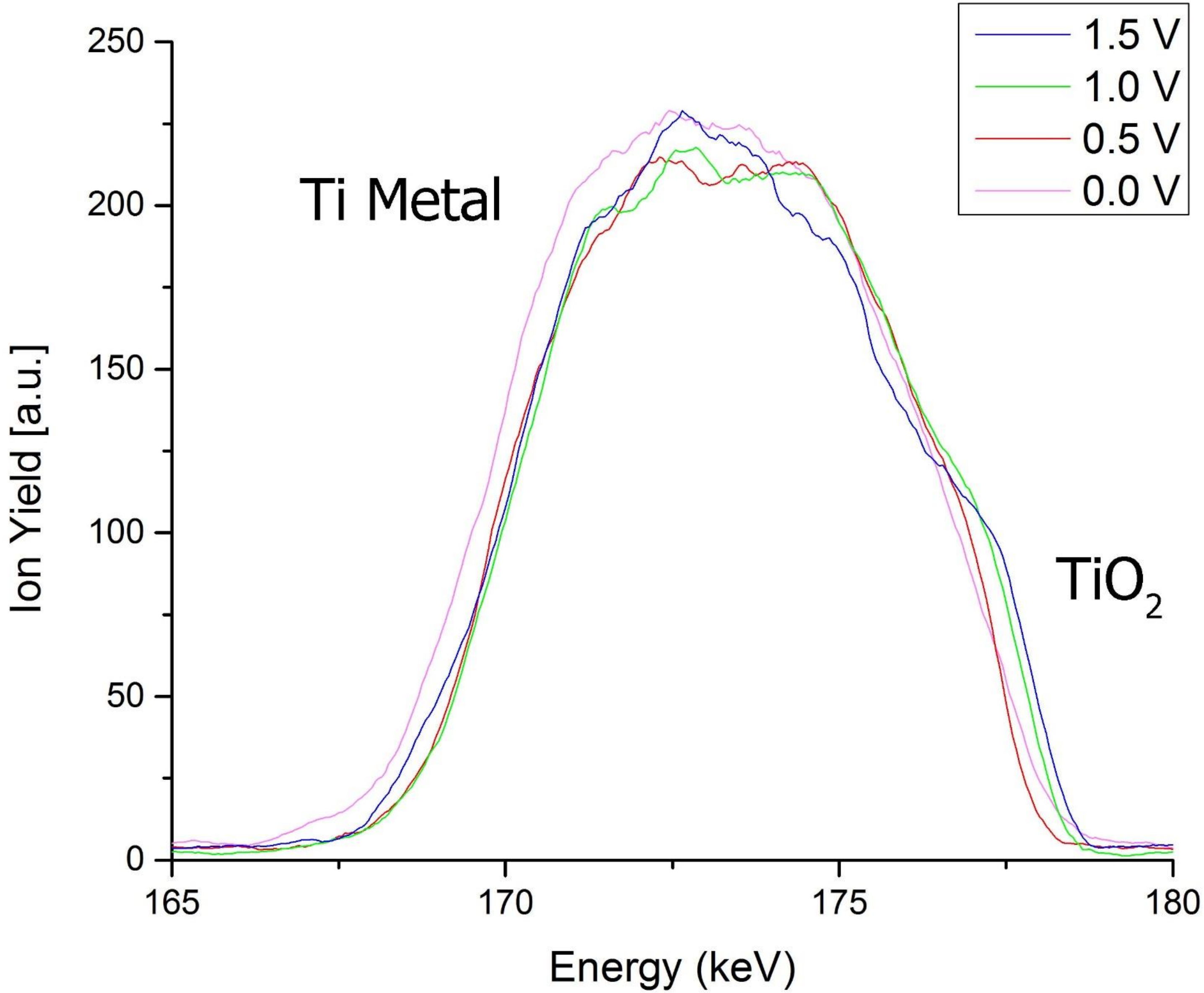


Channeling and blocking in the <111> directions for double alignment.

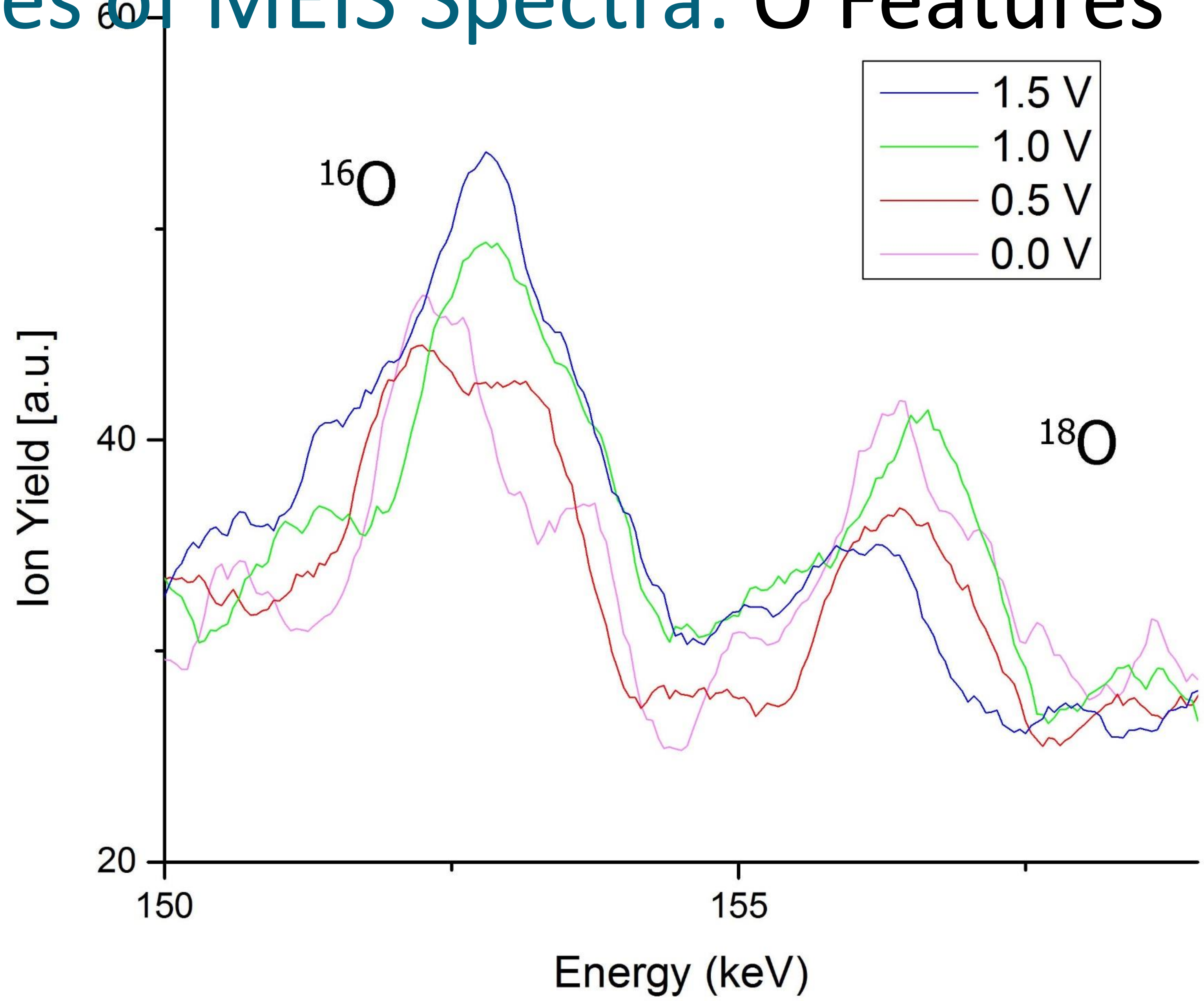
MEIS Full Spectrum



Features of MEIS Spectra: Ti Features

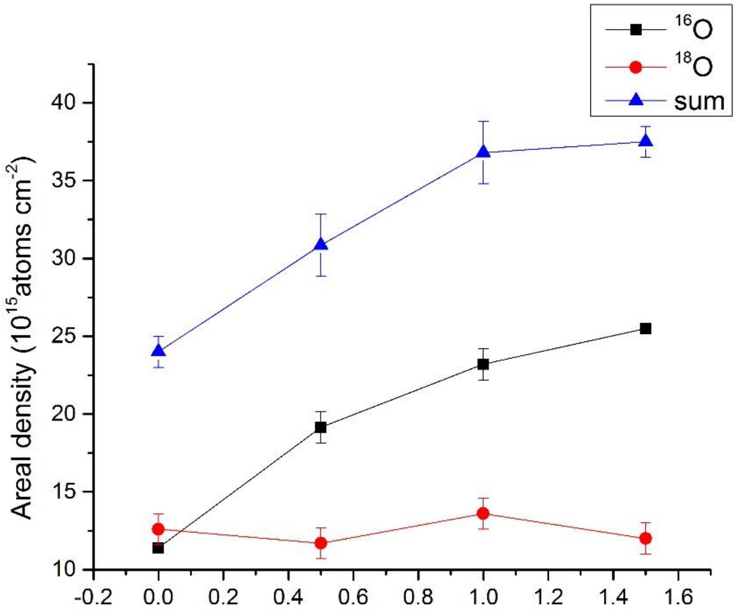


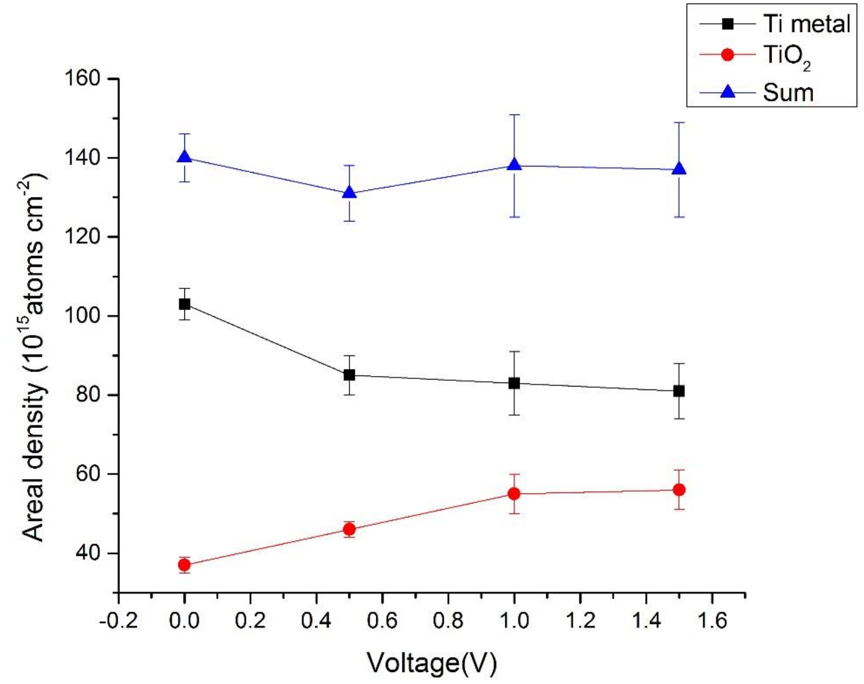
Features of MEIS Spectra: O Features



From Simulations:

Areal density (10^{15}atoms/cm^2)	0 V	0.5 V	1.0 V	1.5 V
Ti	103	85	83	81
TiO_x	37	46	55	56
^{16}O	11.4	19	23	25.5
^{18}O	13	12	14	12





X-Ray Photoelectron Spectroscopy (XPS)

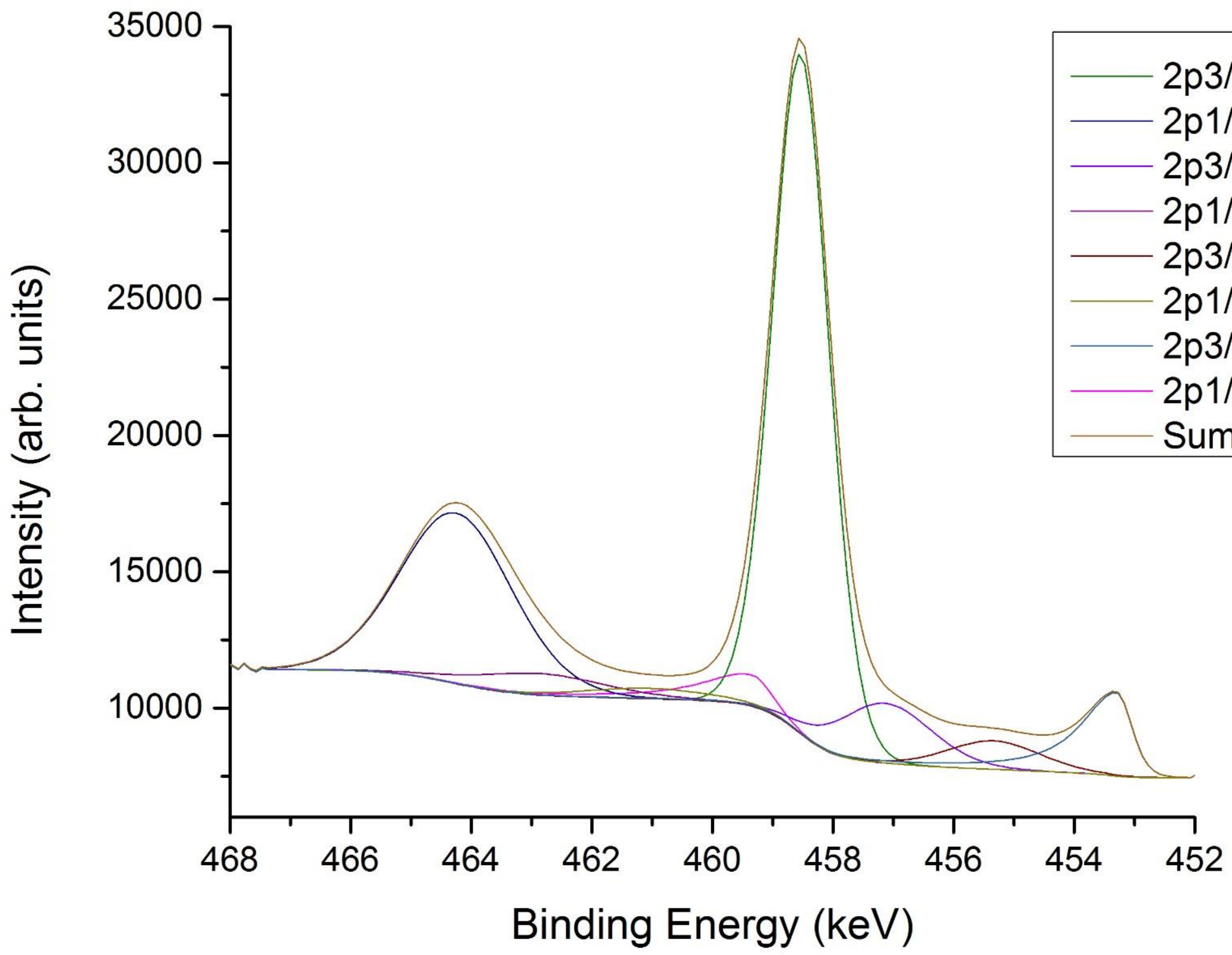
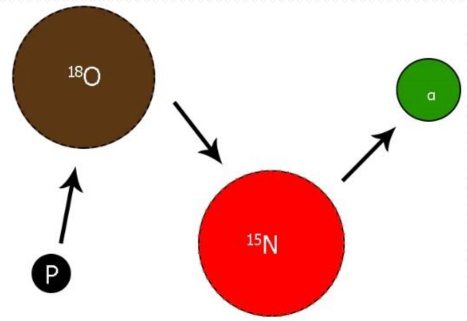
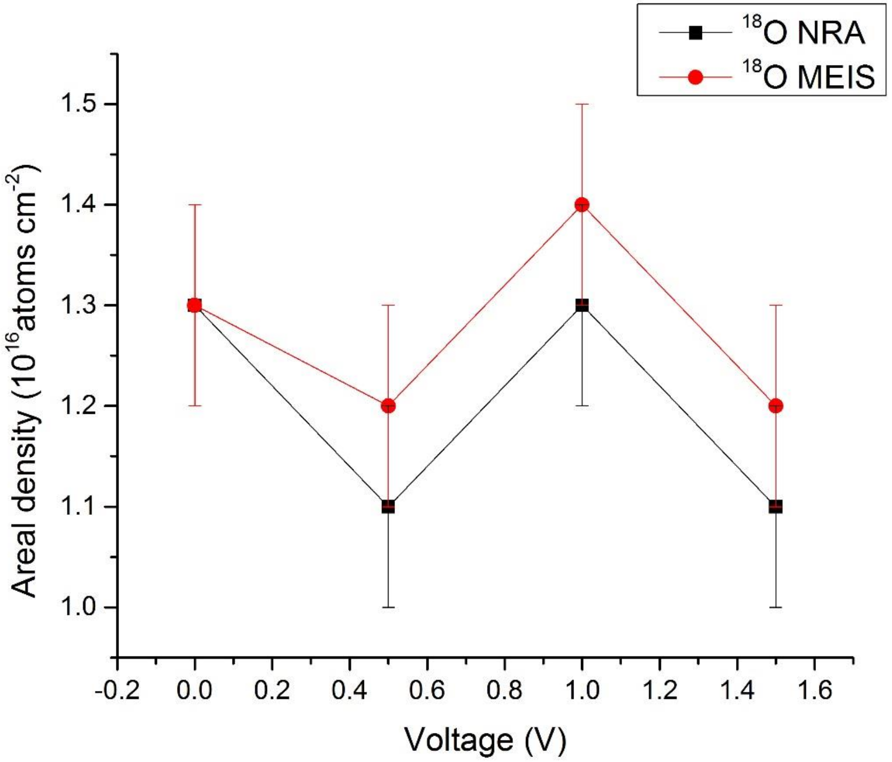
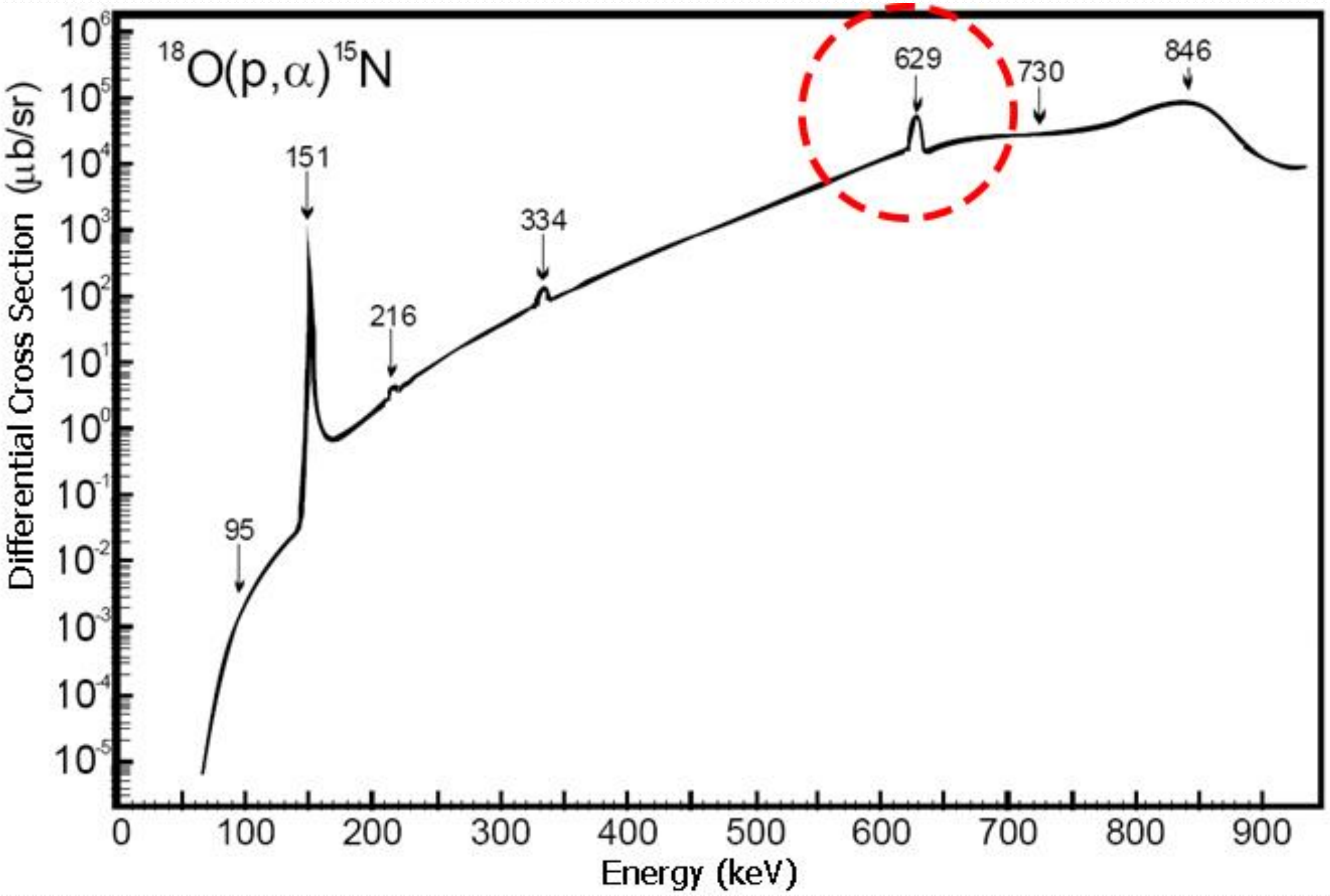


Figure: XPS data of Ti used to justify use of **TiO_2** in simulation. More accurate simulations can take into account different oxidation states

Nuclear Reaction Analysis (NRA): $^{18}O\ (p, \alpha)\ ^{15}N$







Baumvol. *Private correspondence.*

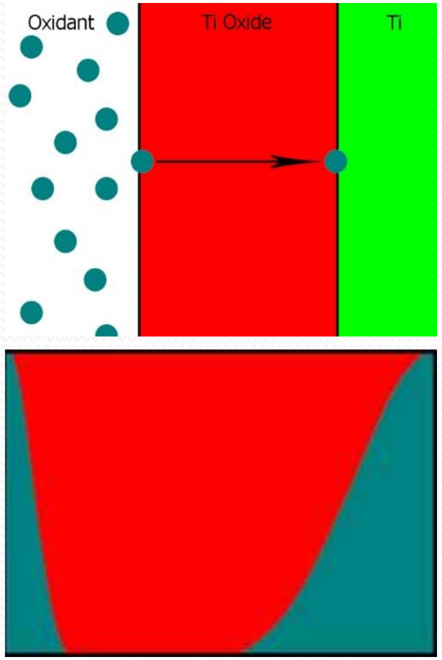
Conclusions

- Oxide growth increases as function of voltage
- Increasing incorporation of ^{16}O towards Ti/Oxide interface:

  -Implies O is the migrating species and not Ti
- Exchange between ^{16}O and ^{18}O minimal

  -Except possibly at oxide surface

Direct oxygen transport (no O-exchange) to interface



Future work

- Oxidation kinetics: with V=const, vary time
- Explore alternative ^{18}O and ^{16}O methods of depth profiling. Particularly the NRA 151keV resonance. Hopefully this matches MEIS.
- Examine importance of morphology