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Application of ERBS analysis on O diffusion in TiO2 films

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Outline

1. Introduction
2. ERBS analysis
3. O diffusion in TiO_2
4. Conclusions

1.

Introduction

ERBS system

Materials characterization

Table 1.1 Imaging and analysis techniques employing electron, ion, and photon beams, with estimates of the achievable spatial resolution

Incident beam	Detected signal	Examples	Resolution (nm)
Electron	Electron	Electron microscopy (TEM, STEM)	0.1
		Electron diffraction (SAED, CBED)	10–1000
		Electron energy-loss spectroscopy (EELS)	<1
		Auger electron spectroscopy (AES)	~2
	Photon	X-ray emission spectroscopy (XES)	2–10
		Cathodoluminescence (CL)	
Ion	Ion	Rutherford backscattering spectroscopy (RBS)	1000
		Secondary ion mass spectrometry (SIMS)	50
		Local electrode atom probe (LEAP)	0.1
	Photon	Proton-induced x-ray emission (PIXE)	500
Photon	Photon	X-ray diffraction (XRD)	30
		X-ray absorption spectroscopy (XAS)	20
		X-ray fluorescence spectroscopy (XRF)	
	Electron	X-ray photoelectron spectroscopy (XPS)	5–10
		Ultraviolet photoelectron spectroscopy (UPS)	1000
		Photoelectron microscopy (PEM or PEEM)	0.5
	Ion	Laser microprobe mass analysis (LAMMA)	1000

Materials characterization

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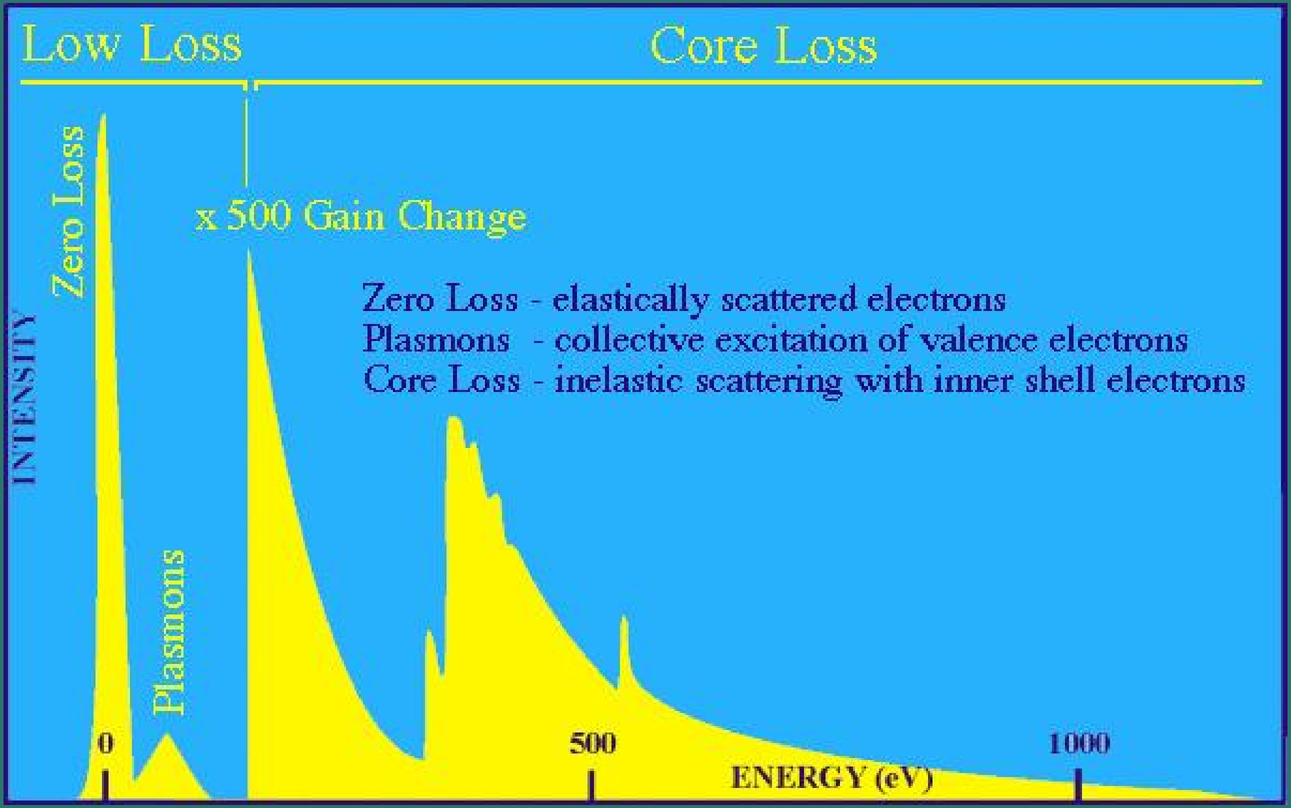
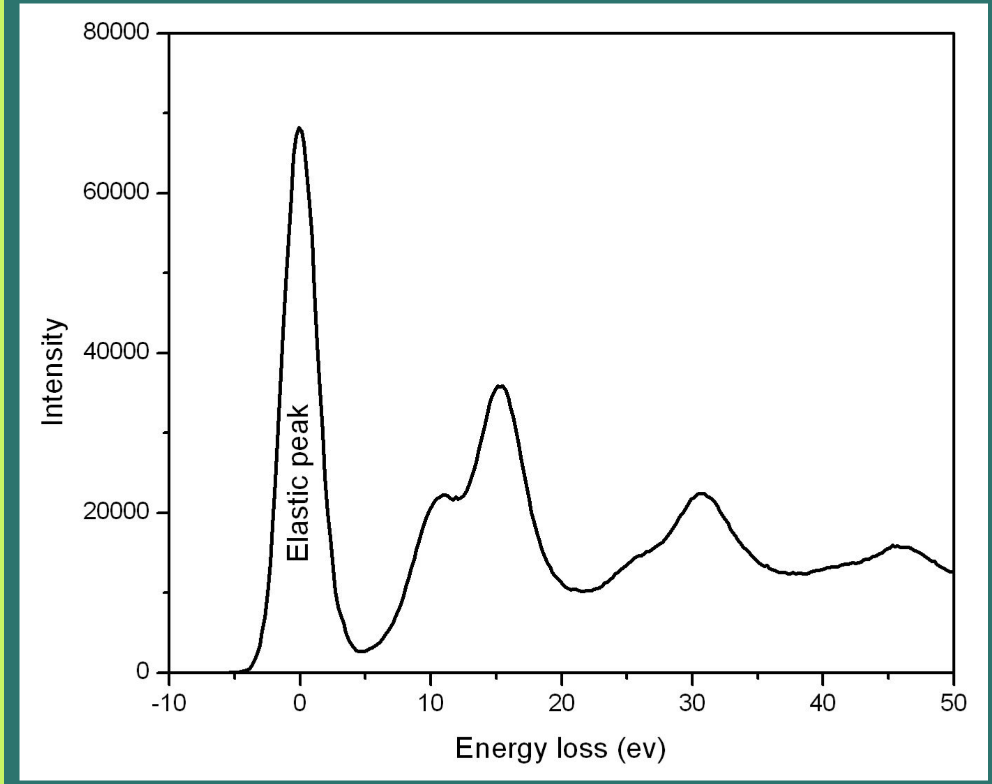
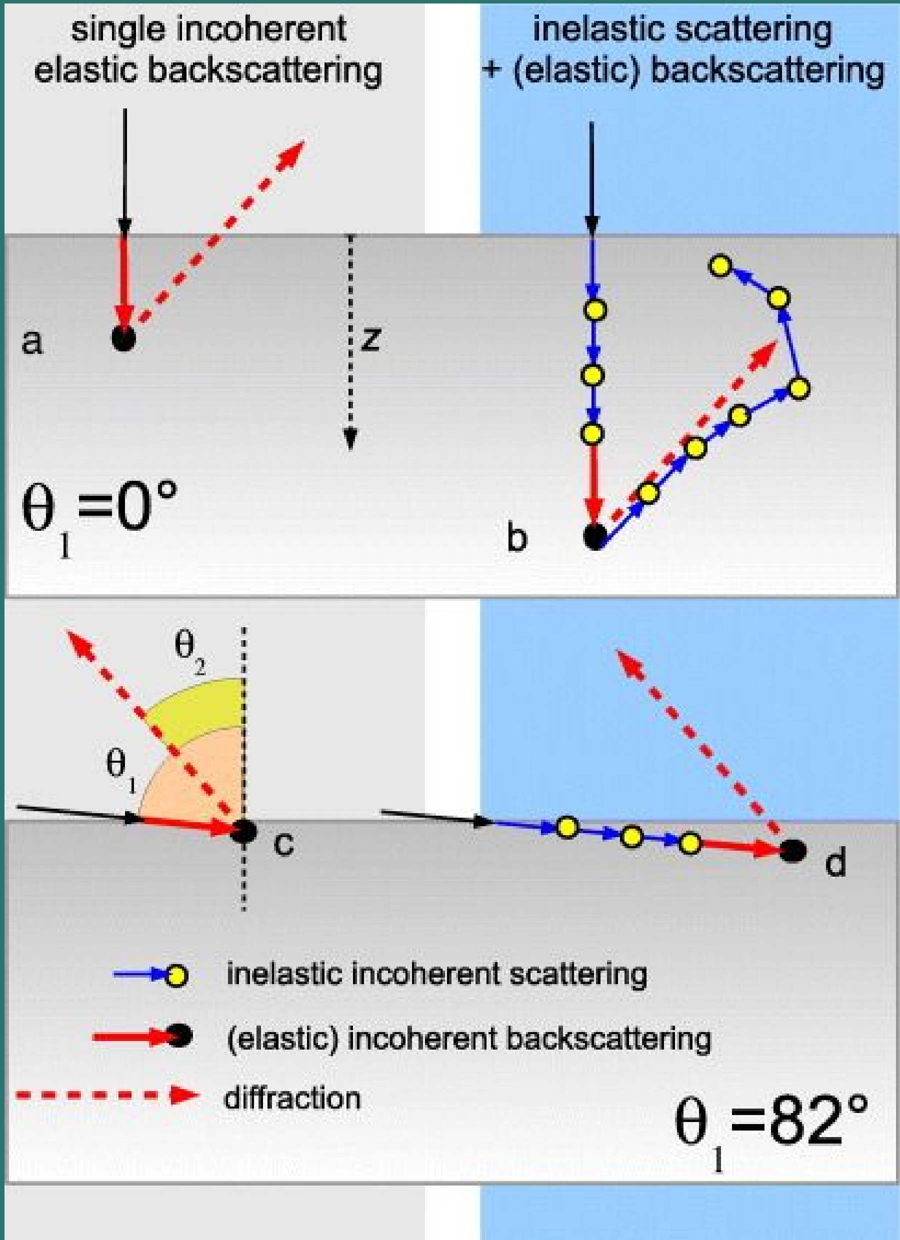
EELS spectrum



Backscattering EELS





Elastic peak

- Kinematic factor

$$E = E_0 - E_r = kE_0$$

$$k \approx 0.9999$$

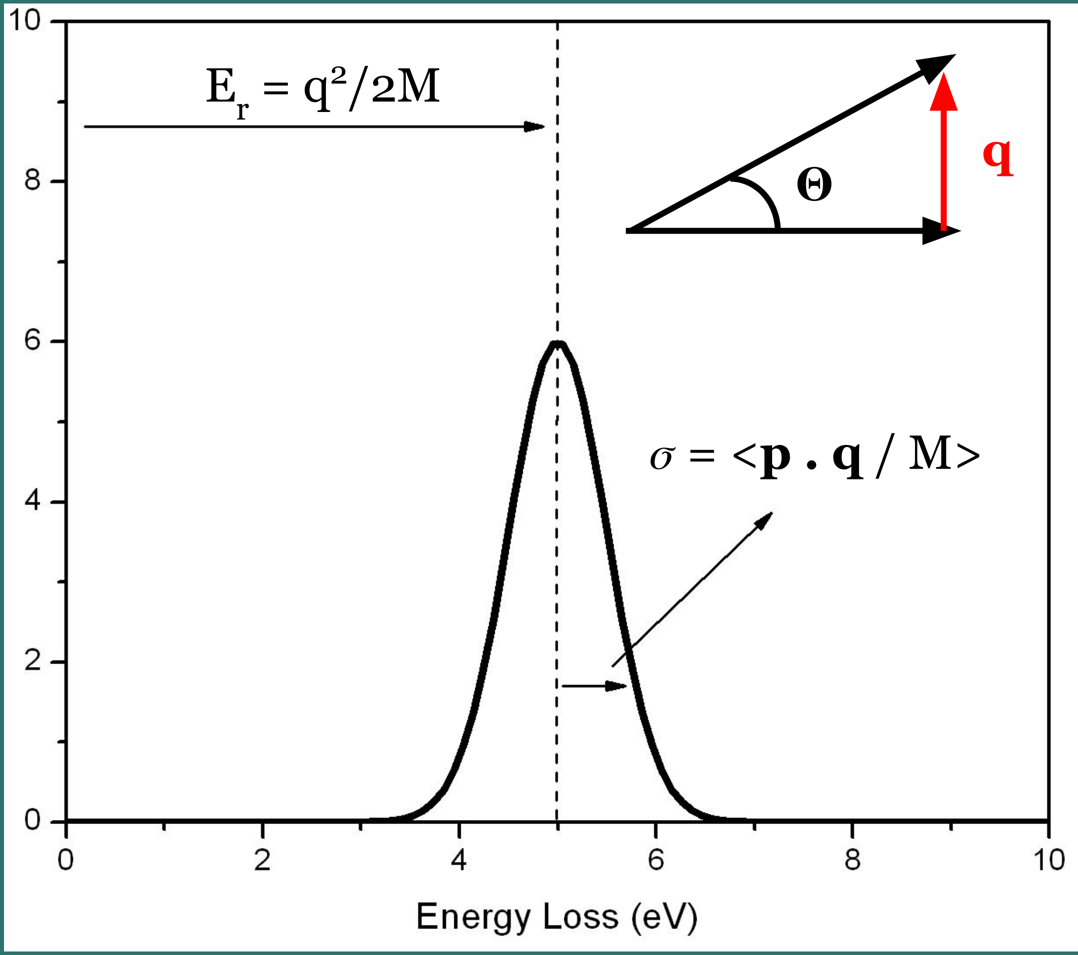
- For isotropic systems

$$\sigma = \left(\frac{4}{3} E_{kin} E_r\right)^{\frac{1}{2}}$$

- Gaussian peak

$$E_r \propto E_0$$

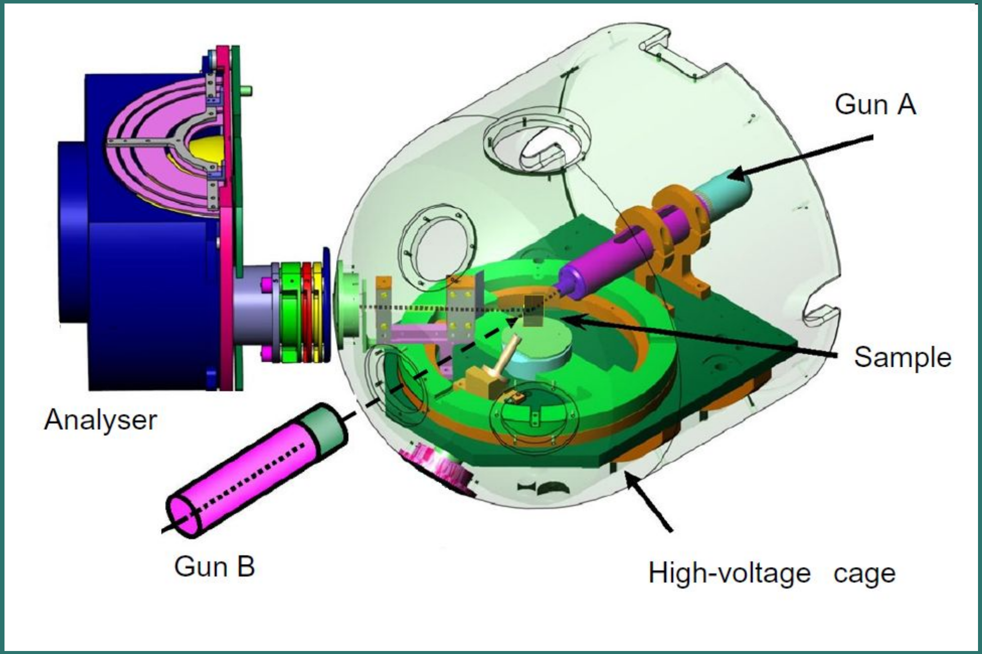
$$\sigma \propto (E_{kin})^{\frac{1}{2}}$$

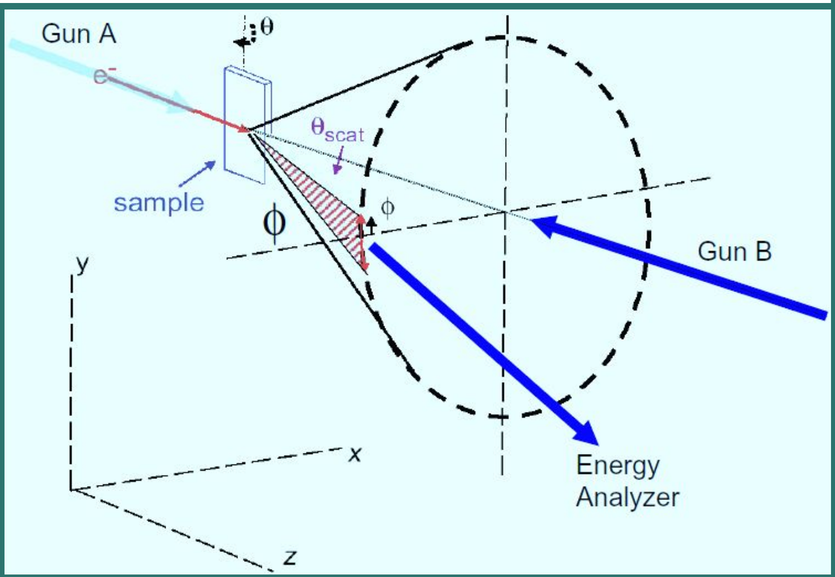


ERBS system at ANU

- 500 eV e-gun
- 40 keV electrons

- High voltage cage
- Hemispherical analyser with ~0.35 eV resolution
- 135º scattering angle





* Went, M. & Vos, M. *Nucl. Instr. Meth. Phys. Res. B,* **2008**, *266*, 998-1011

2.

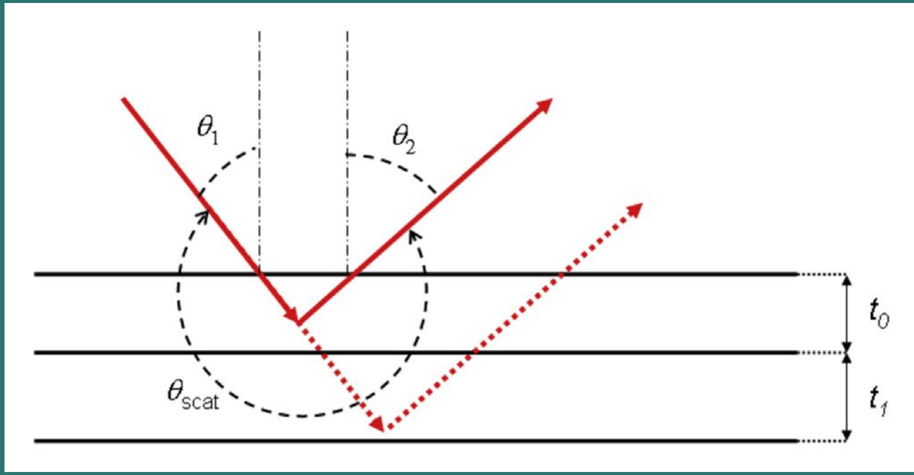
ERBS analysis

Fitting, thickness measurement, multiple scattering

Fitting ERBS's spectra

- First layer contribution

$$I_{i,0} = \gamma\, C_{i,0}\, \sigma_i\, \lambda_0 \left(1 - e^{-\frac{t_0}{(\cos\theta_1 + \cos\theta_2)\lambda_0}}\right)$$

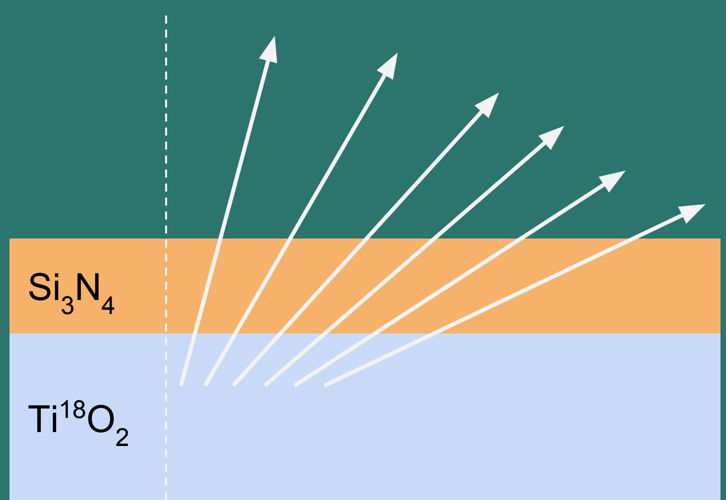


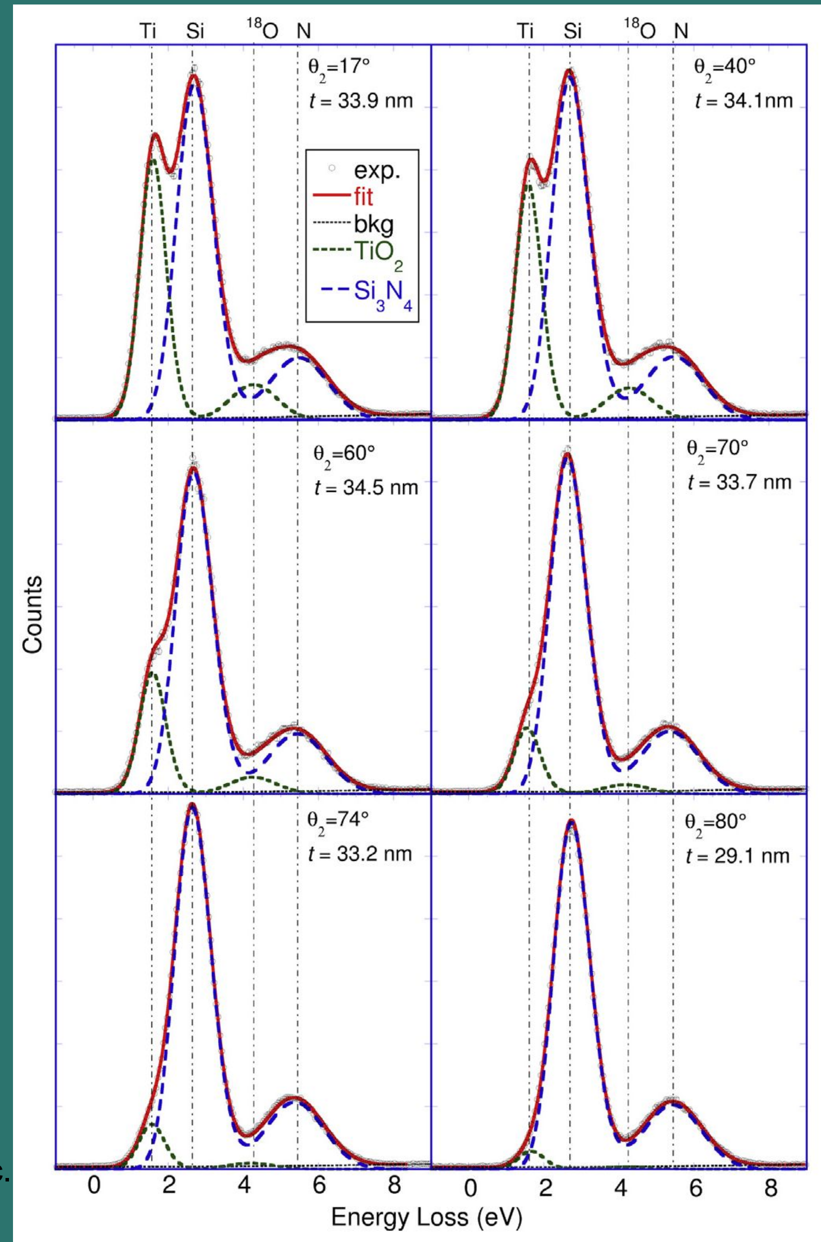
- Second layer contribution is attenuated

$$I_{i,1} = \gamma\, C_{i,1}\, \sigma_i\, \lambda_1 \left(1 - e^{-\frac{t_1}{(\cos\theta_1 + \cos\theta_2)\lambda_1}}\right) e^{-\frac{t_0}{(\cos\theta_1 + \cos\theta_2)\lambda_0}}$$

Thickness measurements

- Exit angle: 17 to 80°
- Displacement → attenuation

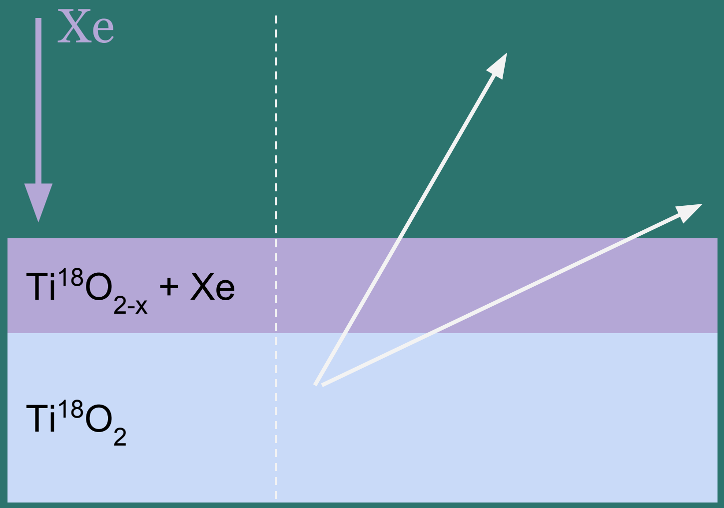


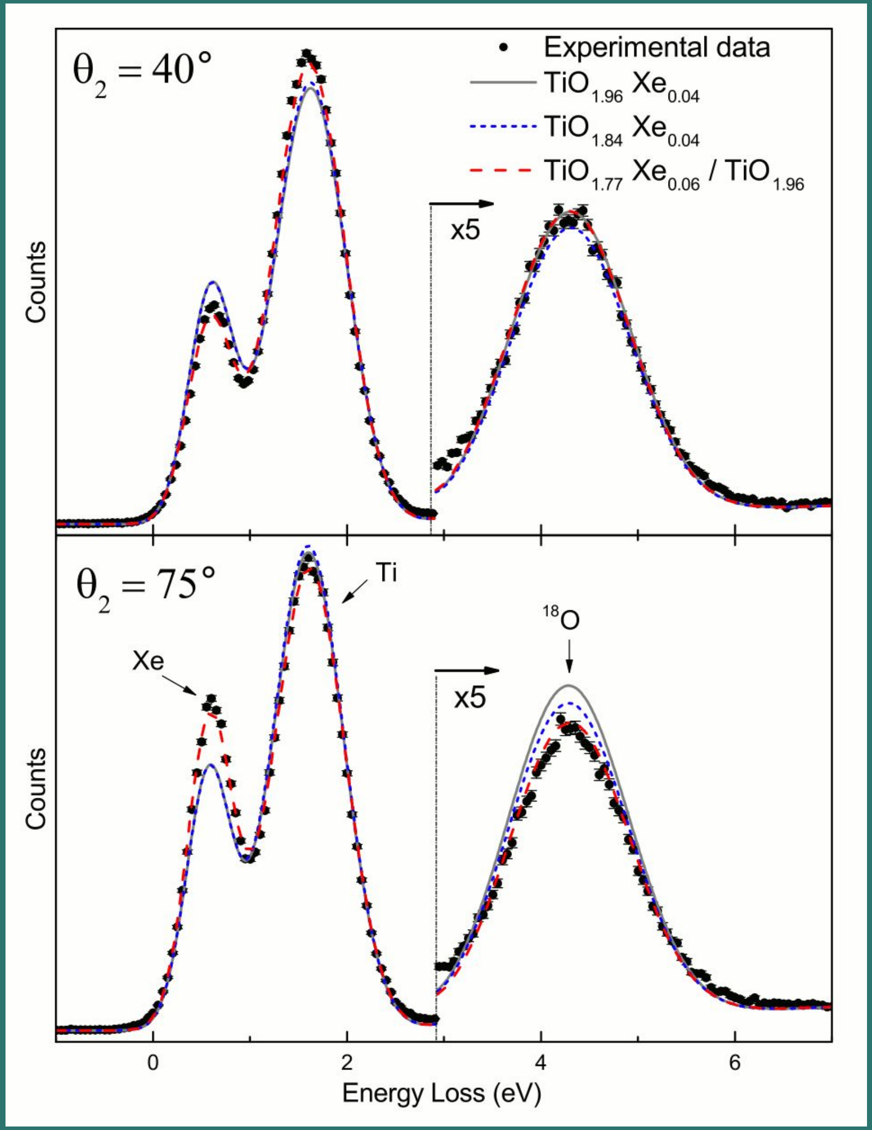


* G.G. Marmitt, L.F.S. Rosa, S.K. Nandi, and M. Vos, J. Electron Spectrosc. Relat. Phenom. 202, p. 26–32 (2015)

Thickness measurements

- Xe sputtering in TiO_2
- Simultaneous fitting
- Preferential sputtering of O





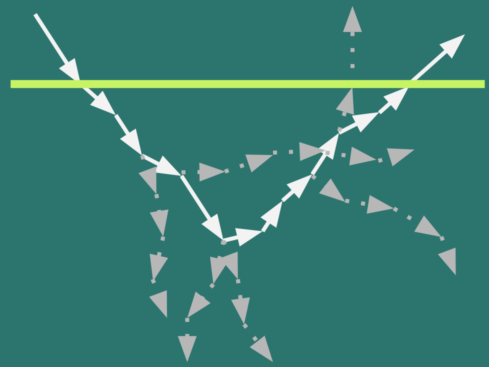
* G.G. Marmitt, L.F.S. Rosa, S.K. Nandi, and M. Vos, J. Electron Spectrosc. Relat. Phenom. 202, p. 26–32 (2015)

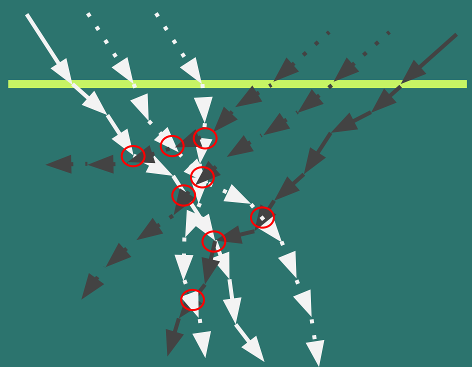
Multiple scattering

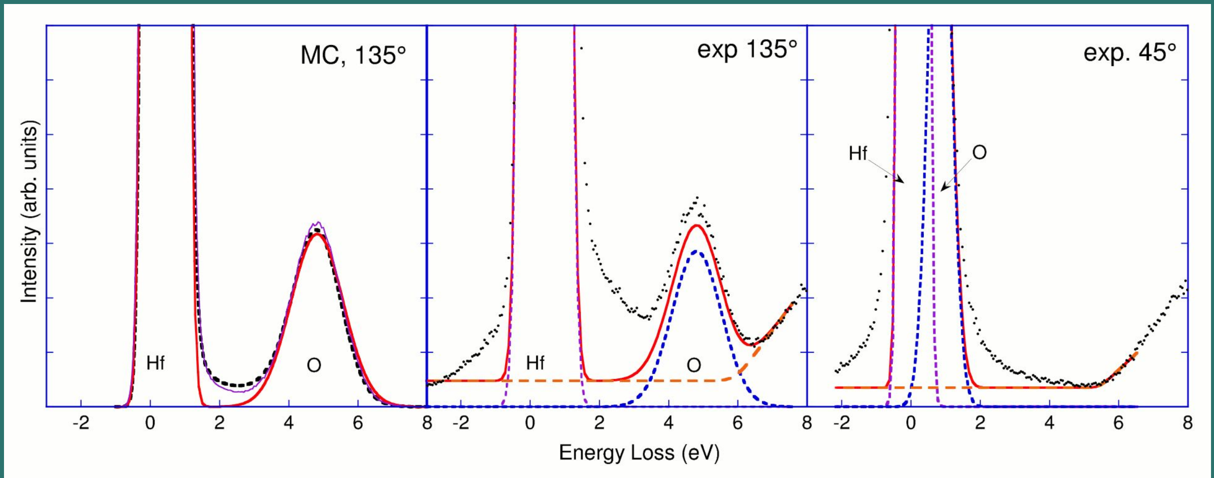
MC direct trajectories ↔ MC connected trajectories

t ~ days

t ~ minutes







* M. Vos, G.G. Marmitt, P.L. Grande. Surface and Interface Analysis, 2016.

3.

O diffusion in TiO_2

Memristors, sample preparation, results

TiO2 Memristor

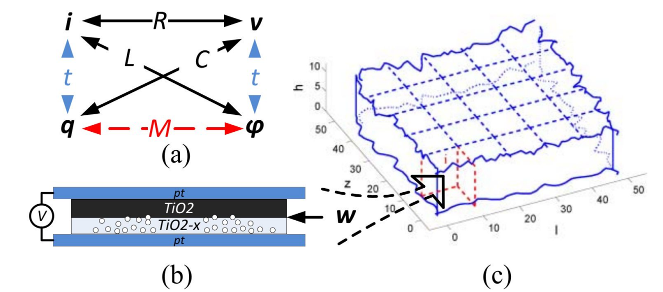
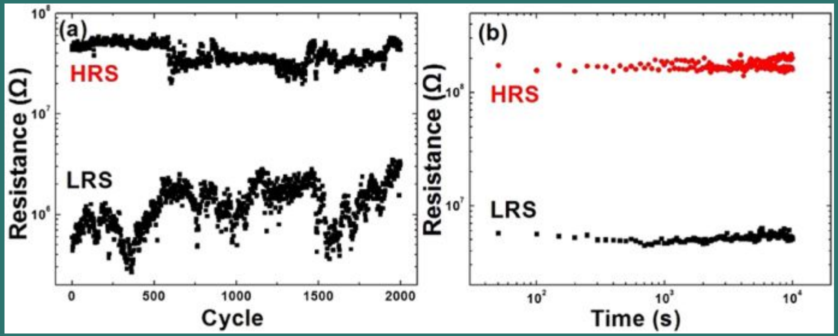
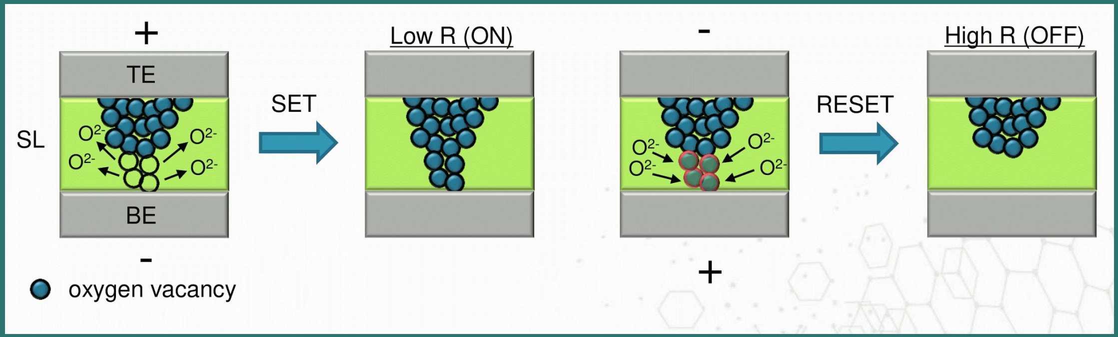
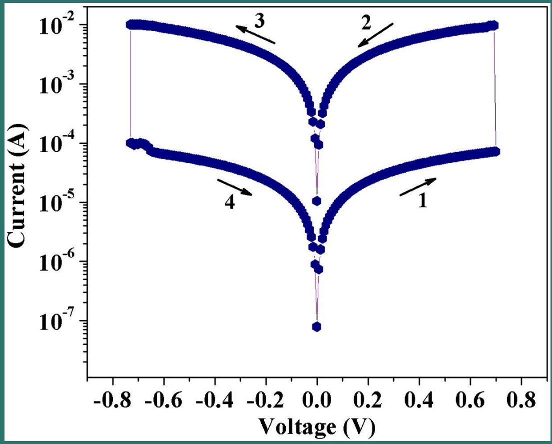


Figure 1. (a) Memristor is the fourth basic circuit element. (b) The ideal TiO_2 memristor model. (c) The geometric variation model.

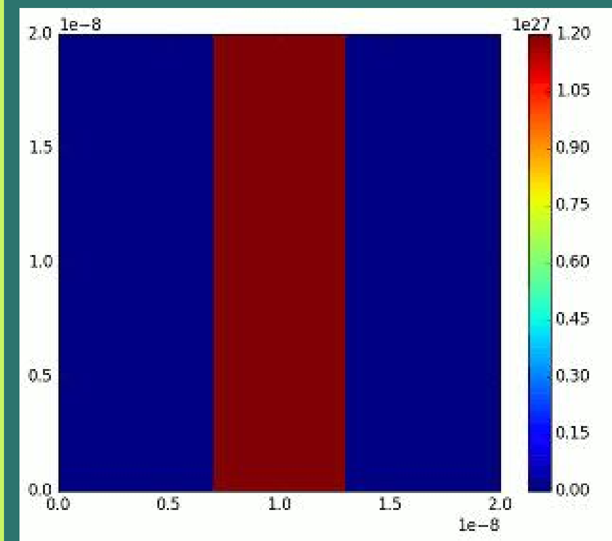




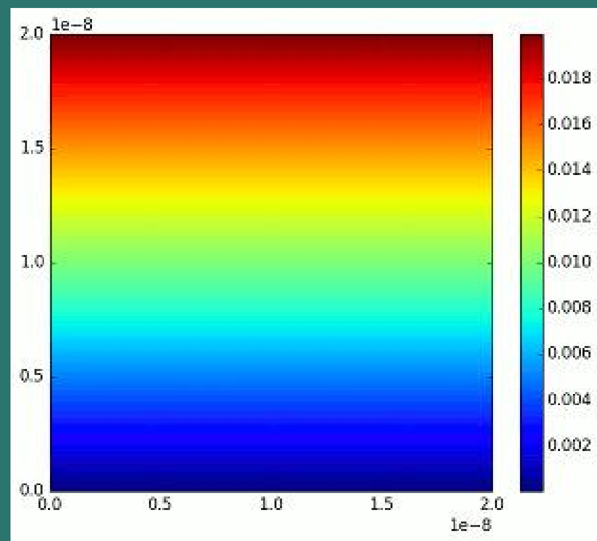


Bipolar switching model

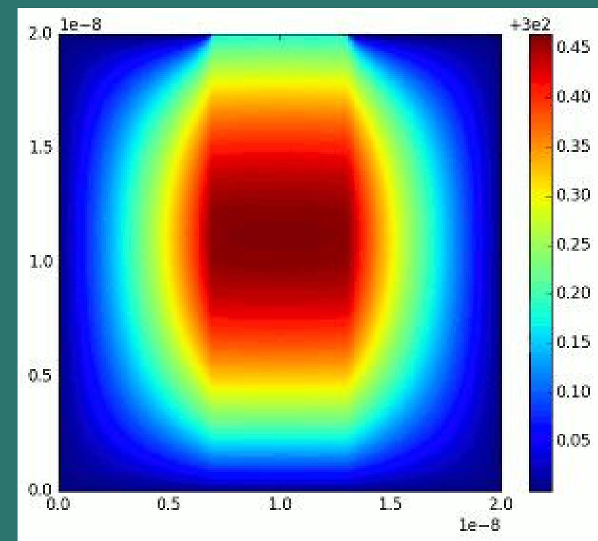
O vacancies



Electric potential



Temperature



$$\frac{\partial n_D}{\partial t} = \nabla \cdot (D \nabla n_D - \mu F n_D).$$

$$\nabla \cdot \sigma \nabla \psi = 0$$

$$-\nabla \cdot k_{\mathrm{th}} \nabla T = \sigma \left| \nabla \psi(r, z) \right|^2$$

$$D = D_0 e^{-\frac{E_A}{kT}}$$

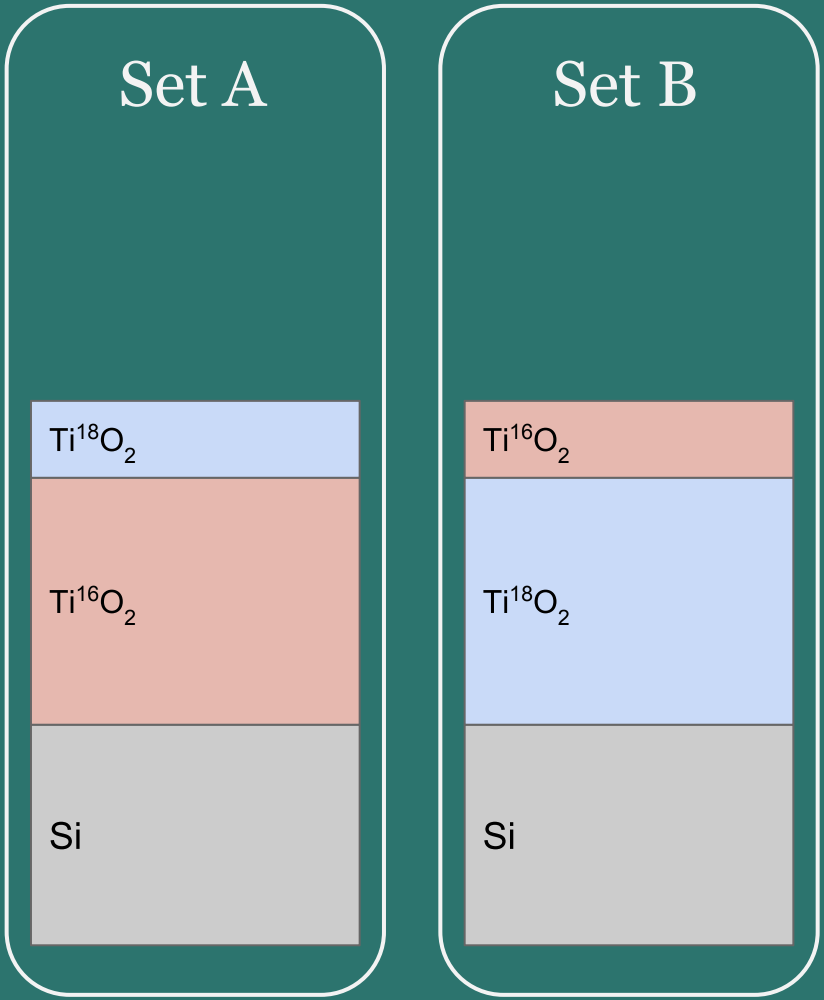
$$\mu = \frac{qD}{kT}.$$

$$\sigma = \sigma_0 e^{-\frac{E_{AC}}{kT}}$$

$$k_{\mathrm{HfO}} = k_{\mathrm{HfO0}} \left(1 + \lambda (T - T_0)\right)$$

Sample preparation

- Depositions (Set A)
  - 60 nm $Ti^{16}O_2$
  - 20 nm $Ti^{18}O_2$
- Inverted sample (Set B)
- Capping layer
- Thermal annealing in Ar
  - 5 - 100 min
  - 500 - 900°C
- HF chemical etching



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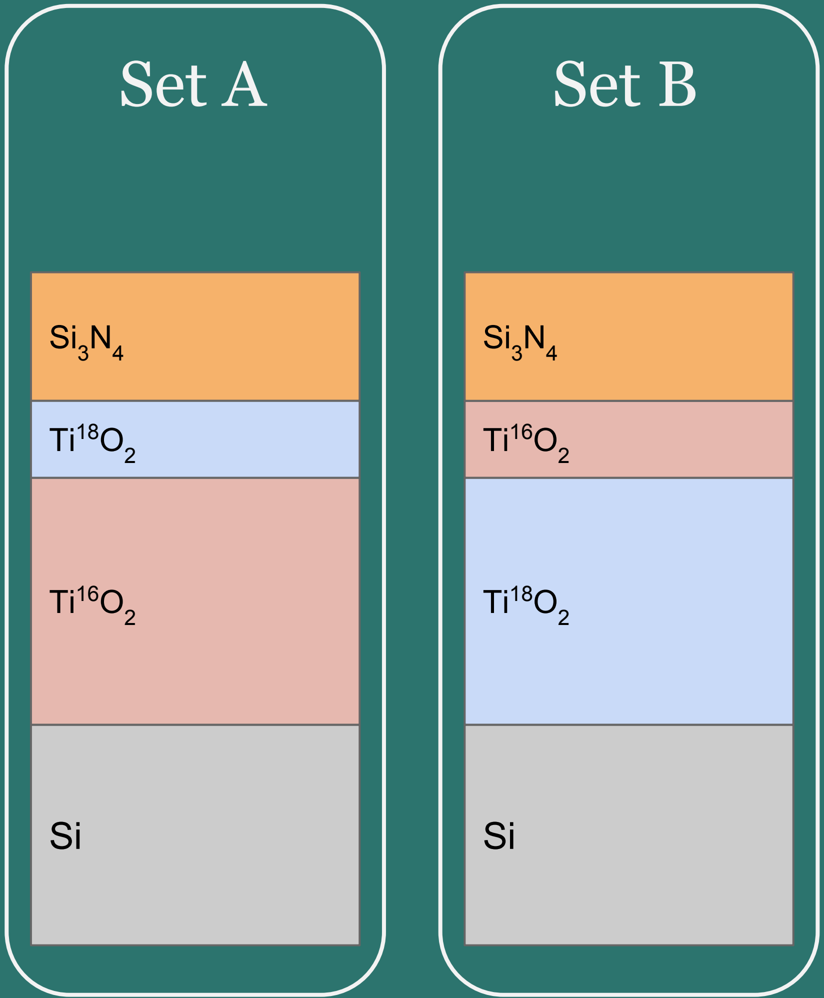

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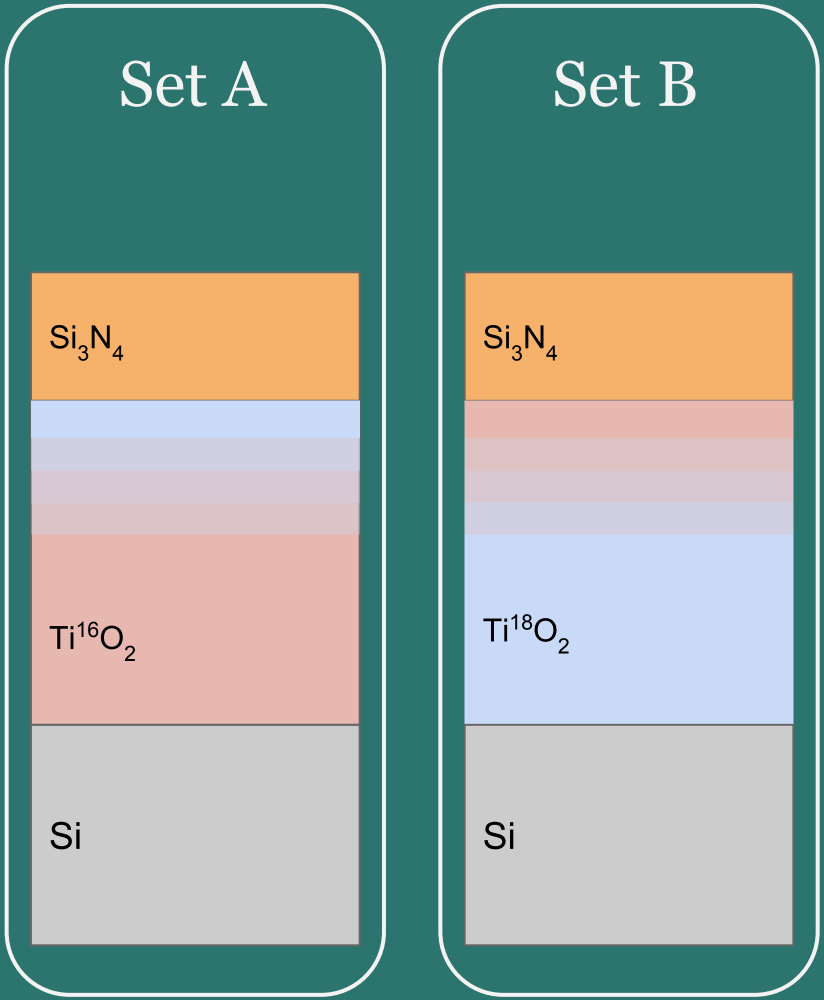

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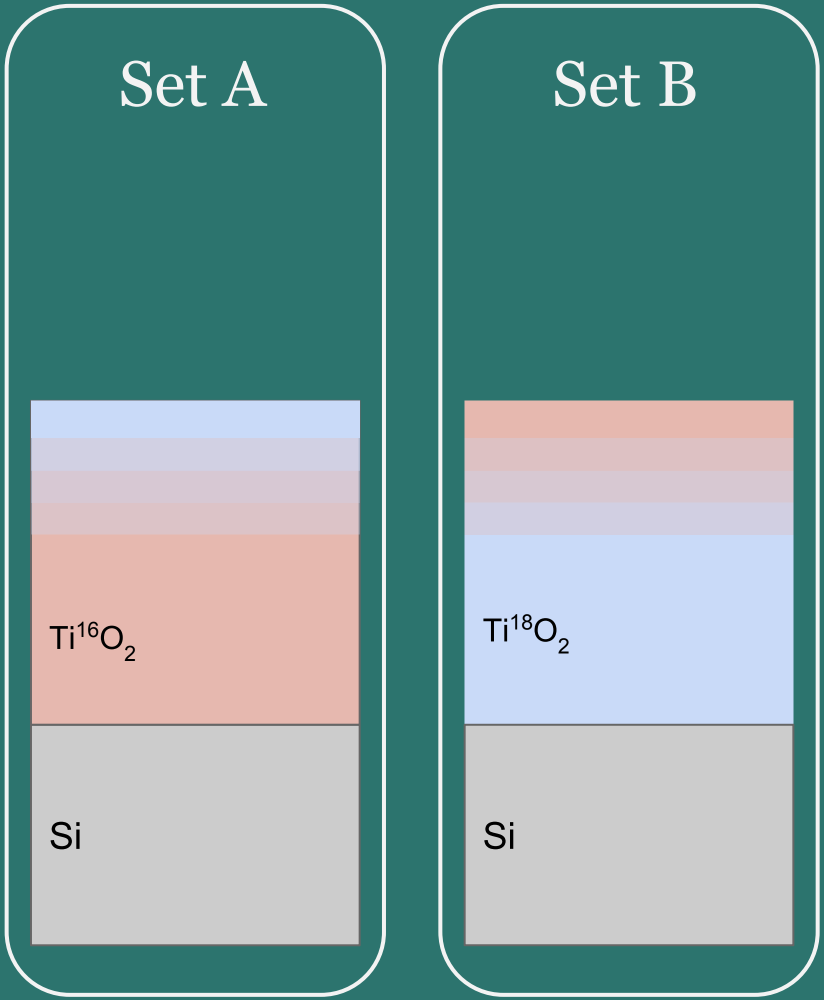
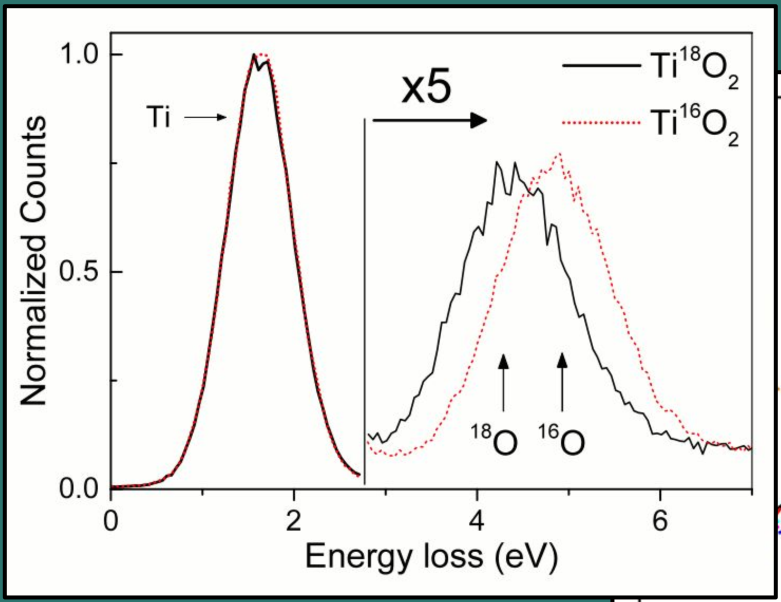
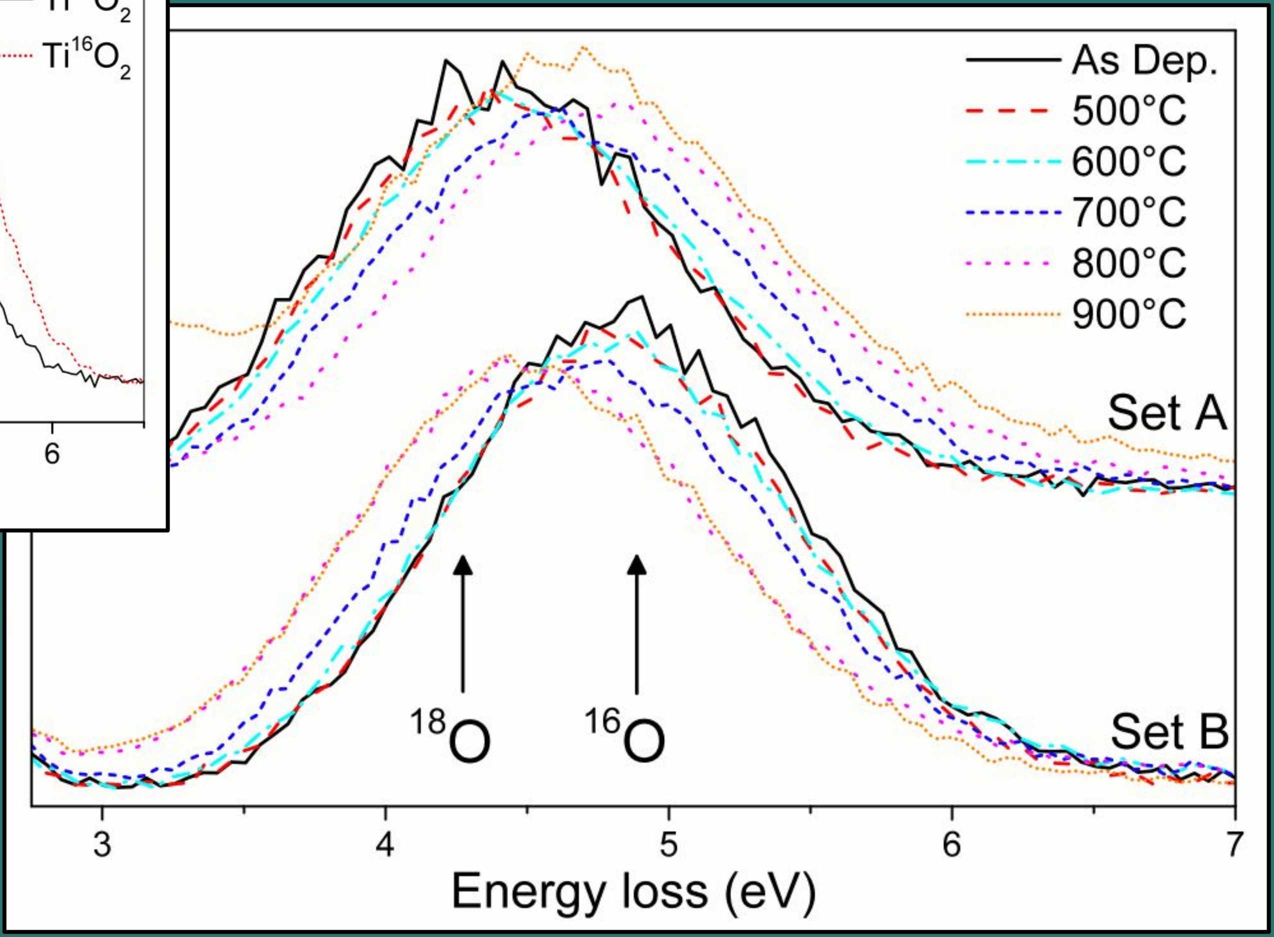
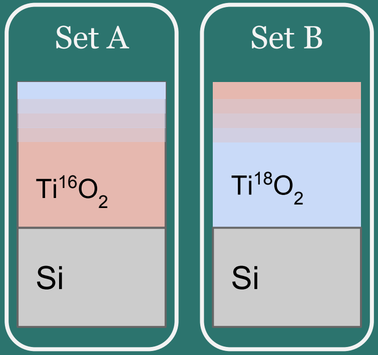


ERBS measurements







40 keV electrons at glancing angles on both sets

Diffusion profile

- Signal intensity

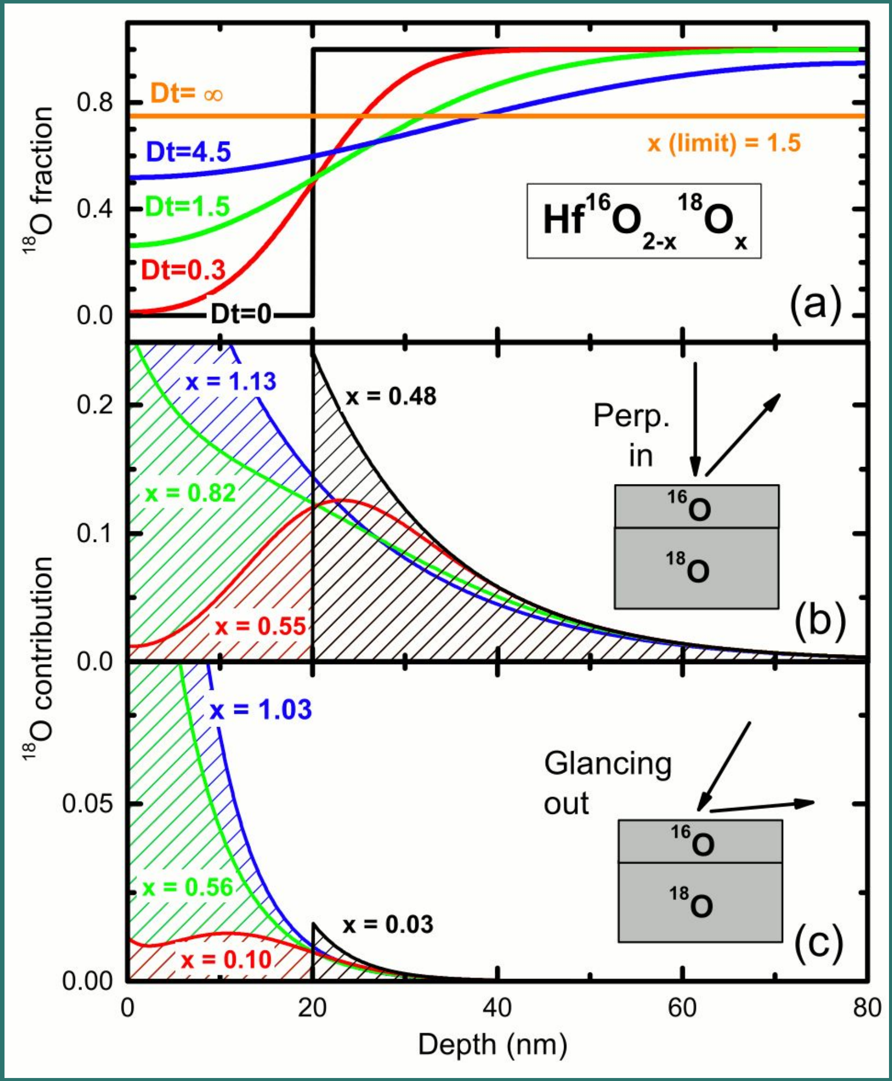
$$I(x) = I_0\, e^{-l(x)/\lambda}$$

- Weighted sum

$$H_i = \sigma_i \int_0^{\infty} I(x)\, \phi_i(x)\, dx$$

- Diffusion equation

$$\frac{\partial \phi_i}{\partial t} = D \nabla^2 \phi_i$$



* M. Vos, P.L. Grande et al. *Phys. Rev. Lett., (APS)*, **2014**, *112*

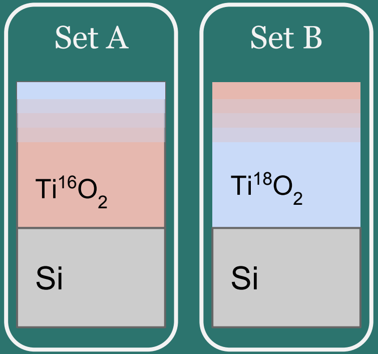
Activation energy

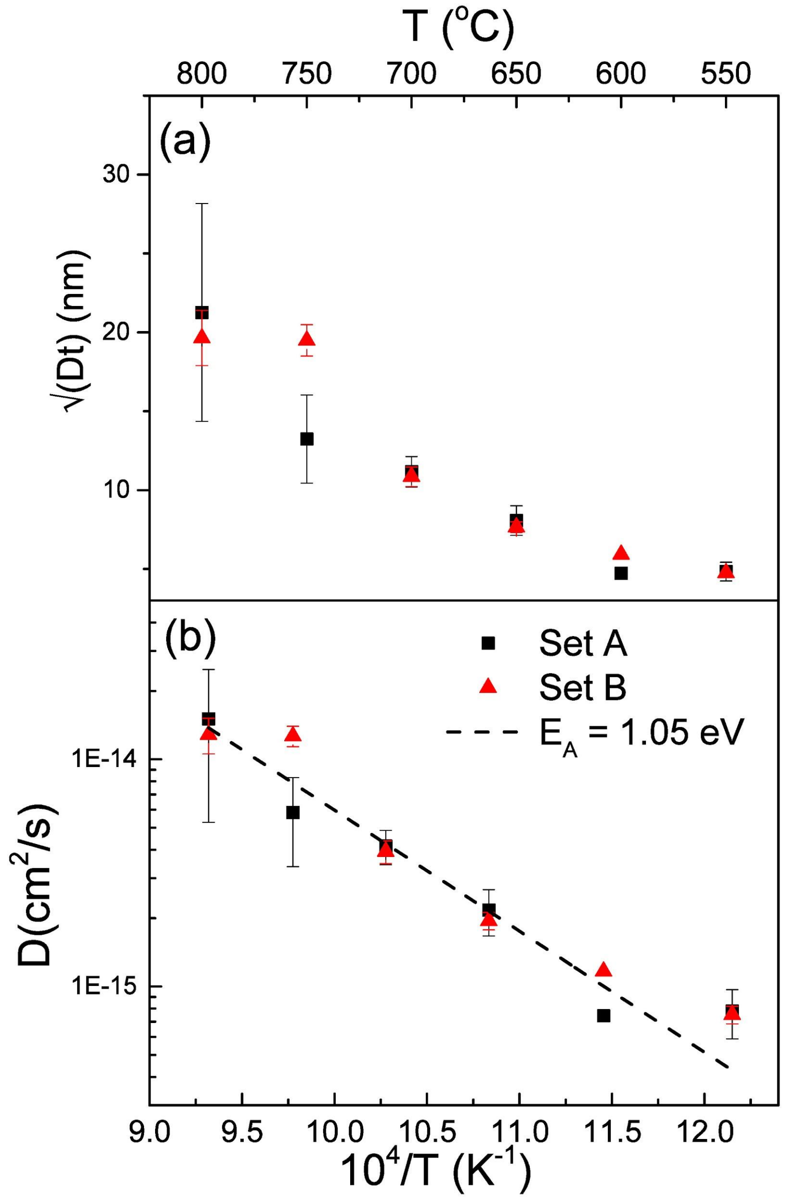
- ERBS spectra fitted with diffusion profiles
- Initial ^{18}O concentration

Slope → E_A for O diffusion in TiO_2

$$D = D_0\, e^{-\frac{E_a}{kT}}$$

$$\ln(D) = \ln(D_0) - \frac{E_a}{k}\,\frac{1}{T}$$



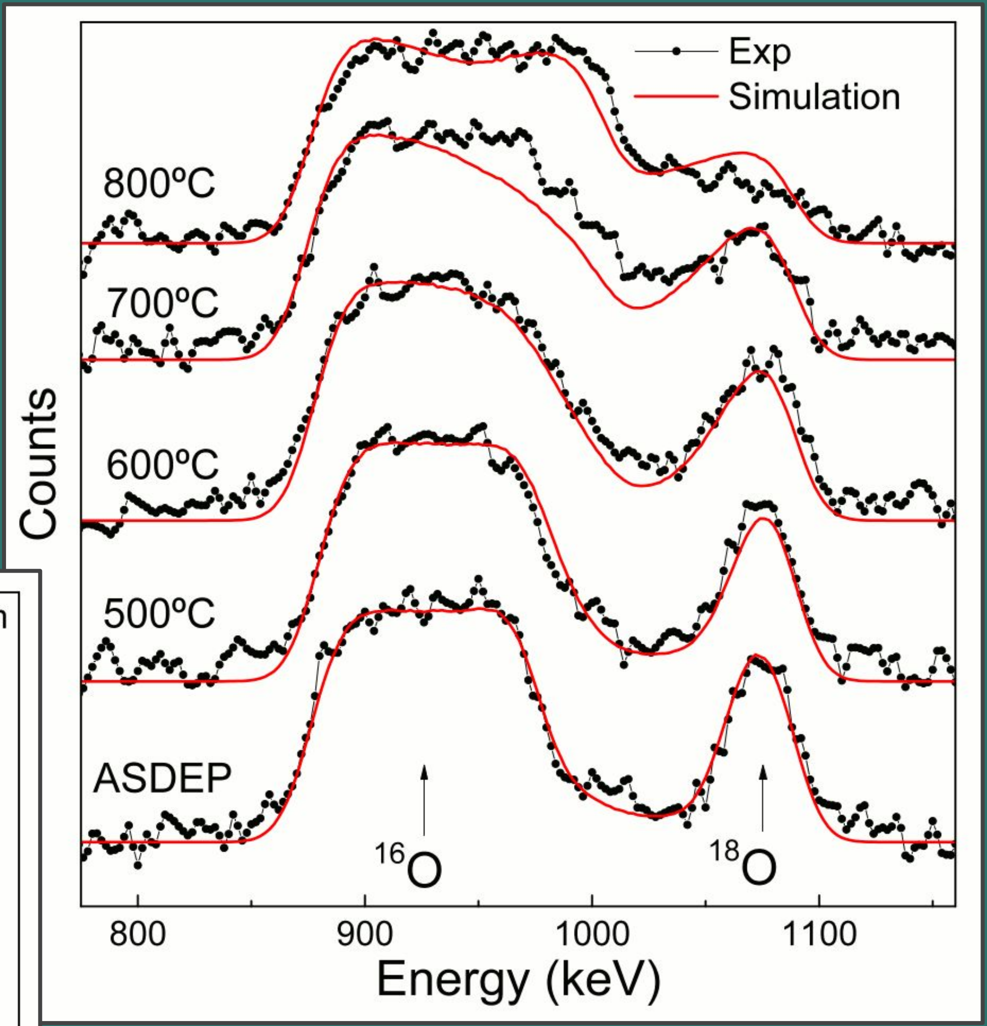


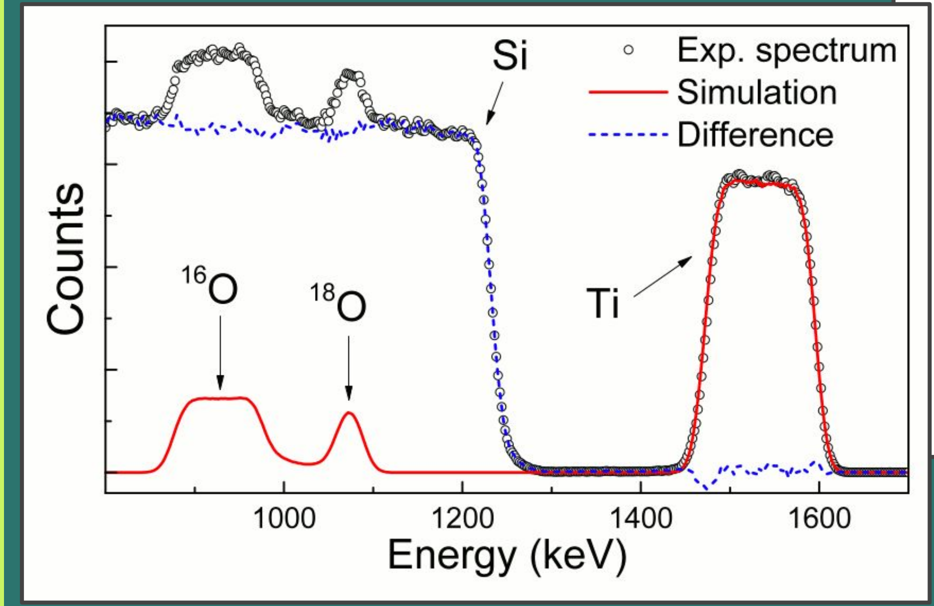
RBS measurements

- 2 MeV He^+
- Only on ^{18}O / ^{16}O / Si

- PowerMEIS simulations

- ERBS's determined profiles





4. Conclusions

Discussion, perspectives

Discussion & perspectives

- ERBS spectra have similarities to RBS and XPS
- Analysis can extract stoichiometry and thickness
- The activation energy of O diffusion in TiO_2 was measured at 1.05 eV
- We are building RRAM devices to further study the formation of the filaments

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Thanks!

CNPq
Conselho Nacional de Desenvolvimento Científico e Tecnológico

CAPES

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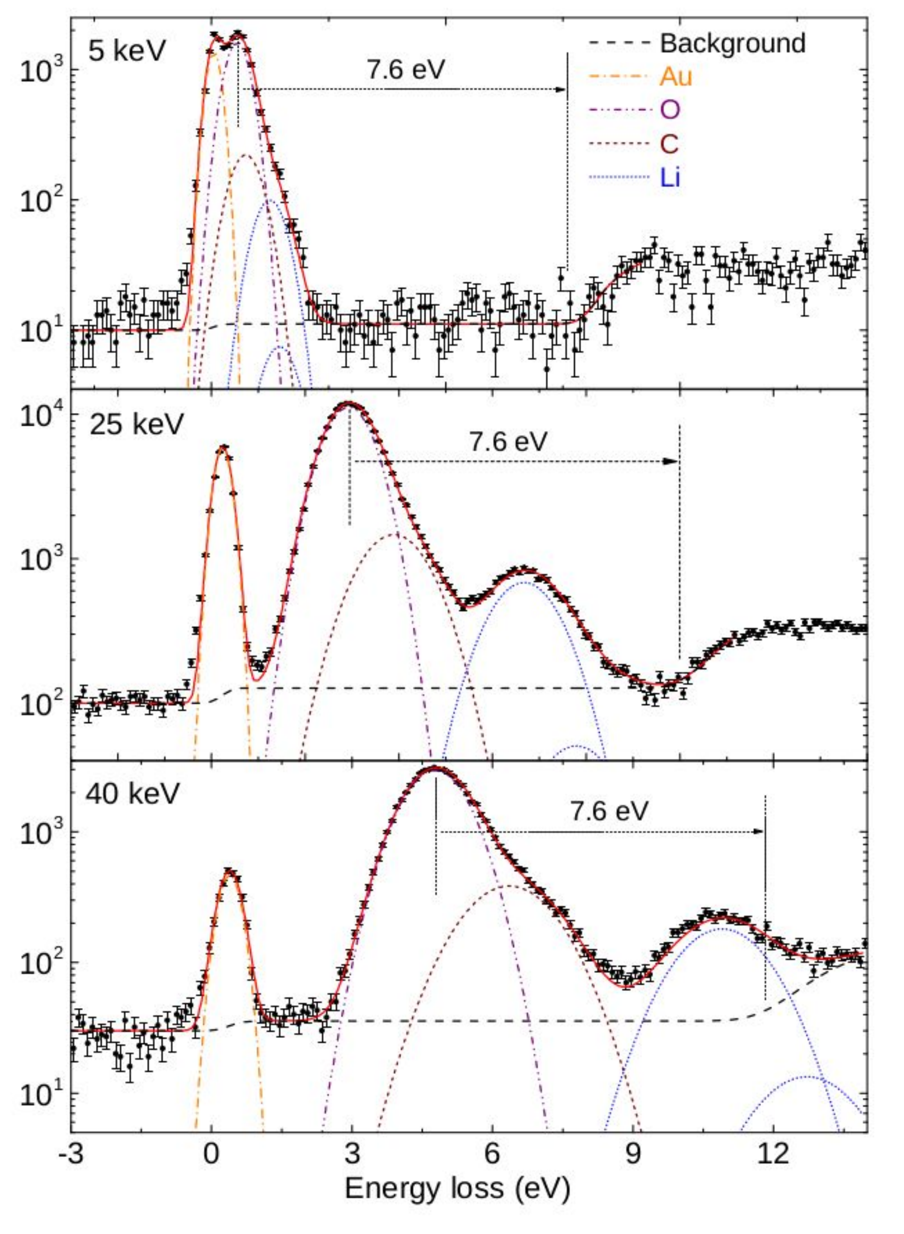
Bandgap

- Au / Li2CO3
- Fixed geometry
- Energy: 5 to 40 keV

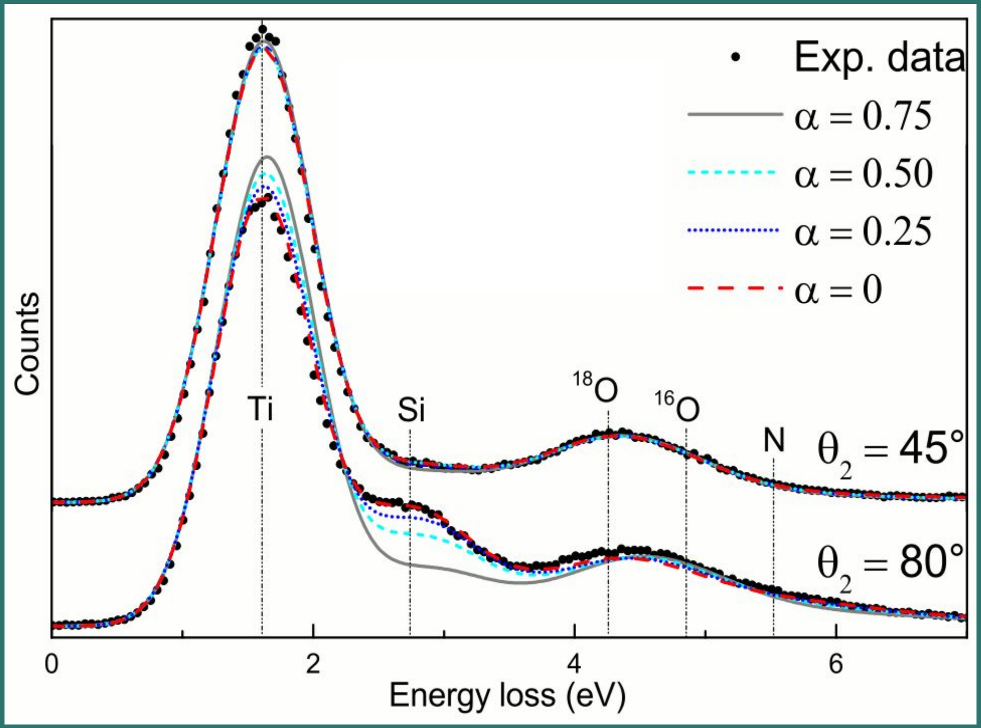
- Simultaneous fitting
- Background → bandgap

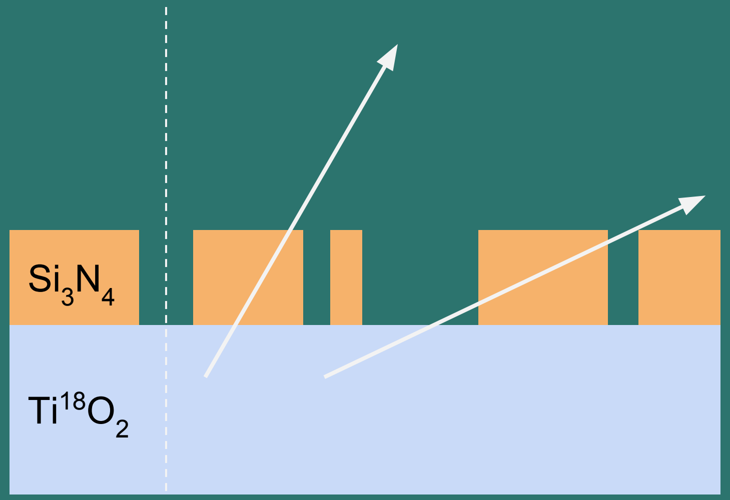


* M. Vos, G. G. Marmitt, Y. Finkelstein and R. Moreh. The Journal of Chemical Physics, v. 143, n. 10, p. 104203, Sep 2015.

Thickness measurements

- Scatt. angle: 135°
- Si_3N_4 islands?





$$\alpha = 1 - \frac{A_{Si_3N_4}}{A_{total}}$$

* G.G. Marmitt, L.F.S. Rosa, S.K. Nandi, and M. Vos, J. Electron Spectrosc. Relat. Phenom. 202, p. 26–32 (2015)

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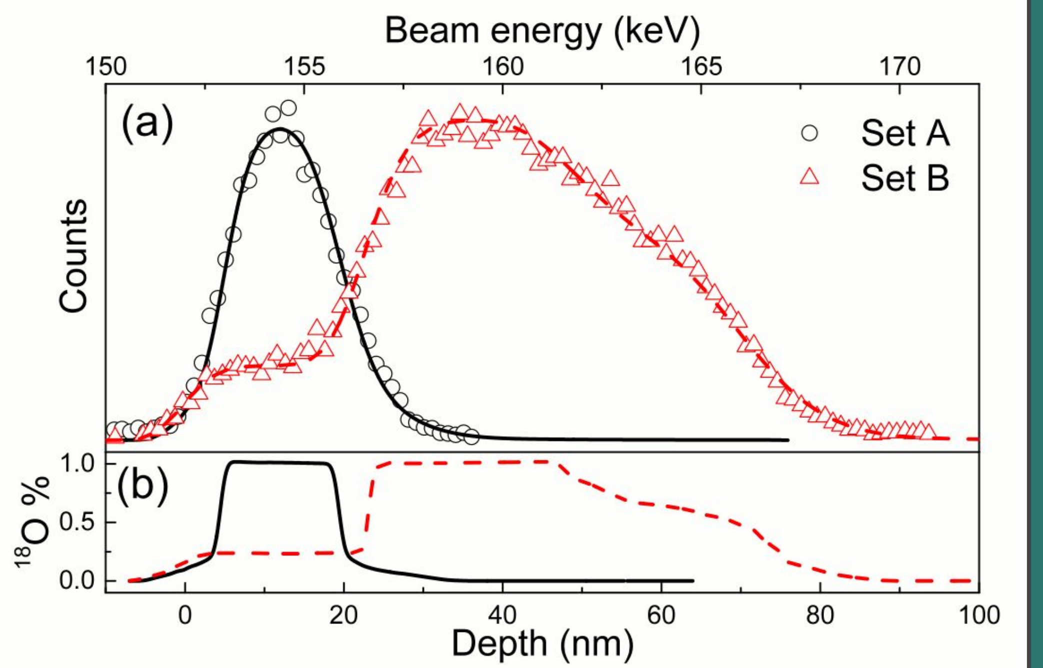
Set A

Set B



NRP: 151 keV resonance $^{18}O(p, \alpha)^{15}N$

Diffusion irregularity

Our measurements	Arita et al.
500 °C < T < 800°C	T > 1000°C
t = 5 min	t > 20 h
E_A ~ 1.05 eV	E_A ~ 3 eV