NATIOMEM

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Reduced preferential sputtering of TiO_2 (and Ta_2O_5) thin films through argon cluster ion bombardment.

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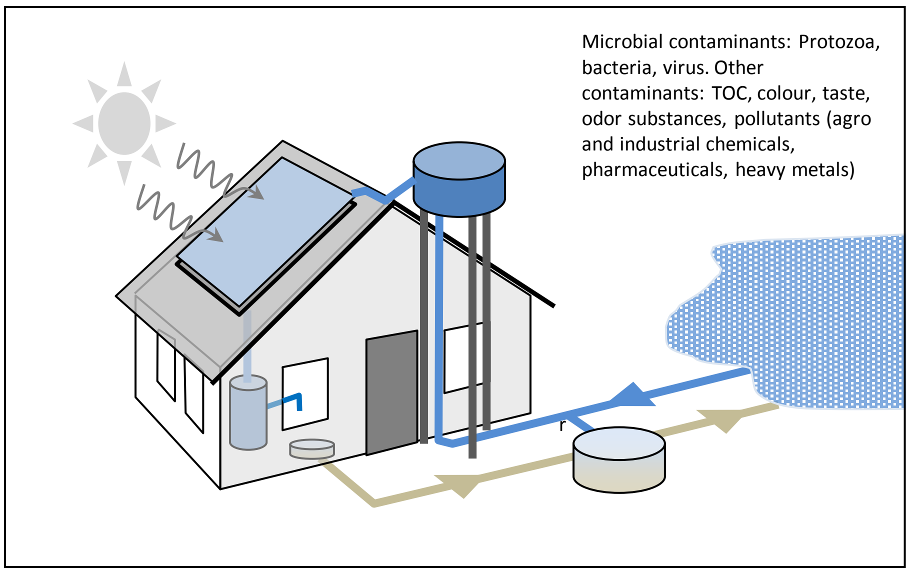
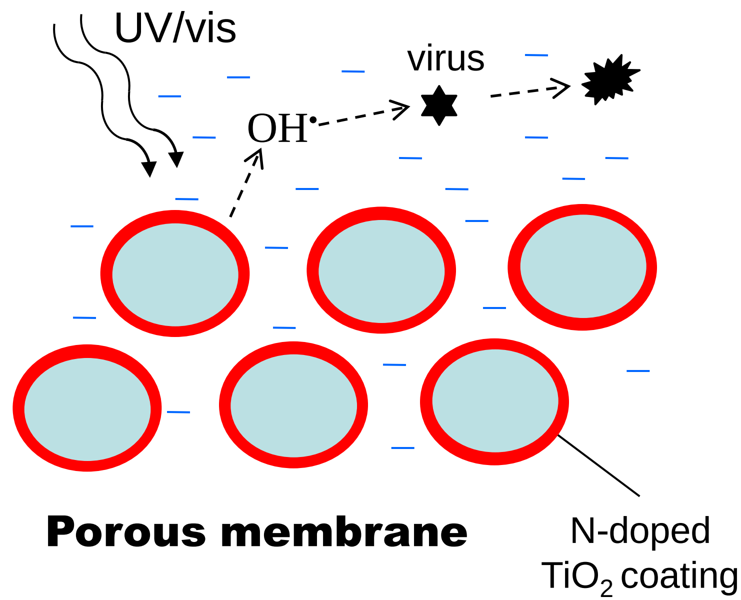
NATIOMEM – EU project

NAno-structured TION Photo-Catalytic MEMbranes for Water Treatment

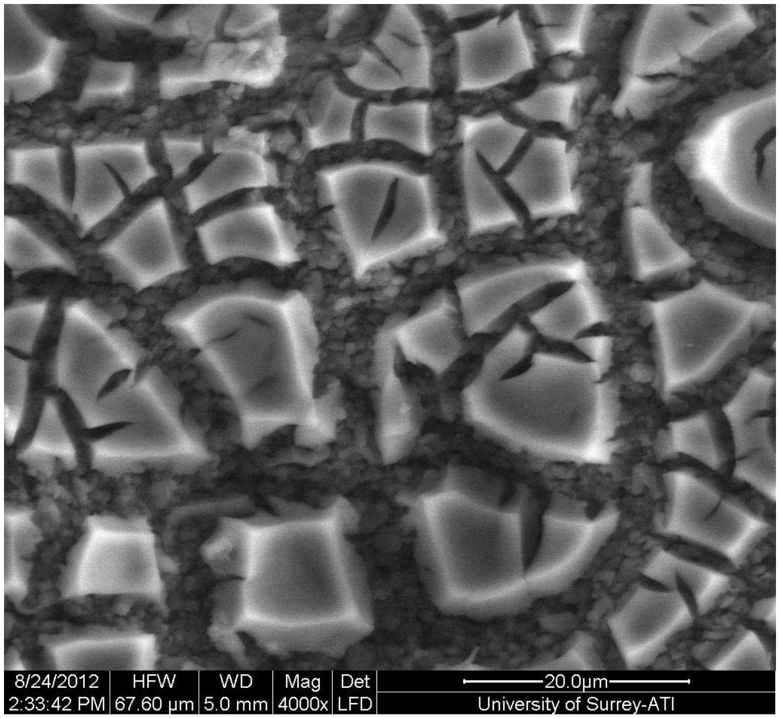
Overlall objective: develop a nanostructured catalytic membrane that will be a cost effective component in solar radiation based treatment systems for converting surface or waste water into drinking water using membrane substrates coated with nanostructured photocatalytic N-doped TiO_2 thin films.



Photocatalysis

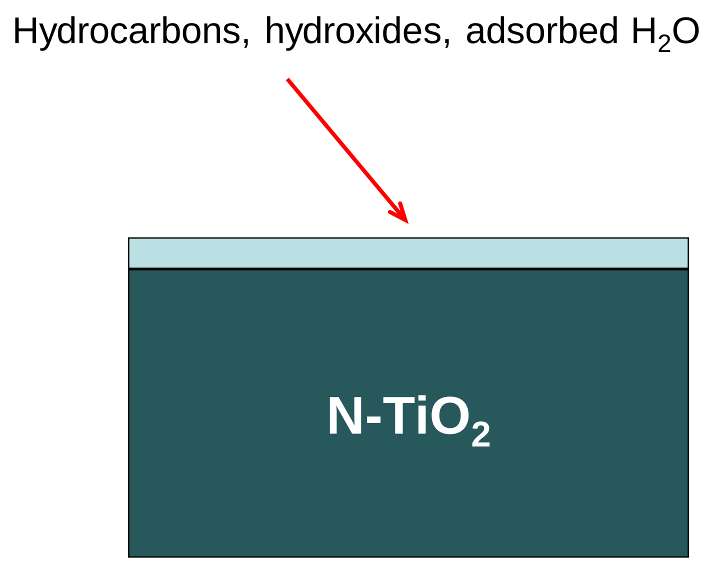


XPS analysis employed to accurately determine N-doped TiO_2 thin film composition (sol-gel, FVAD, sputtering)



N-doped TiO_2 film deposited on alumina membrane by sol-gel

Contaminant species at surface interfere with the analysis and are removed through Ar^+ ion sputtering prior to XPS spectral acquisition



Preferential sputtering

Preferential sputtering → One component sputtered in preference to the other(s) → - Surface binding effects
- Mass difference effects

Affected oxides: Preferential removal of O atoms

Ti, Ta, Co, Ni, Cu, Nb, Ru, Ag, W, Pb, Bi, Hf

Ion source

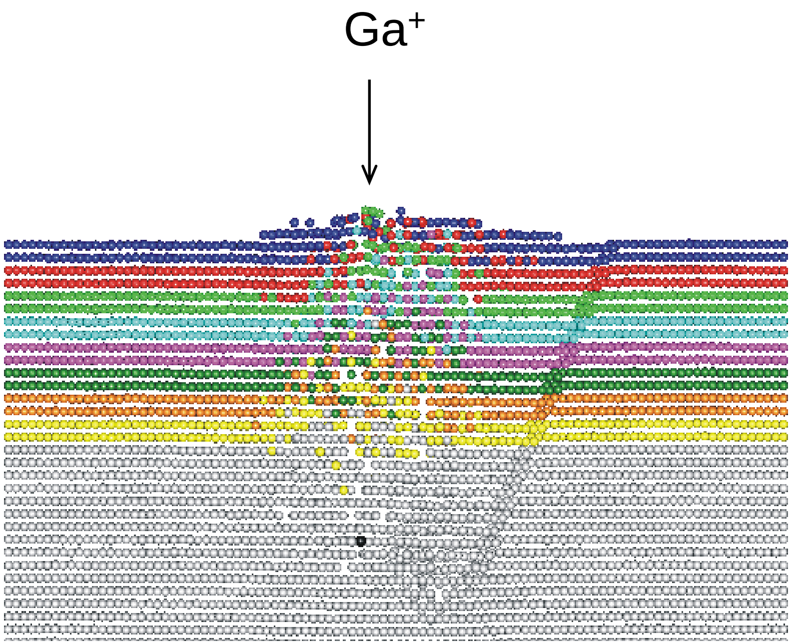
$\mathbf{Ar^+}$

Alternatives

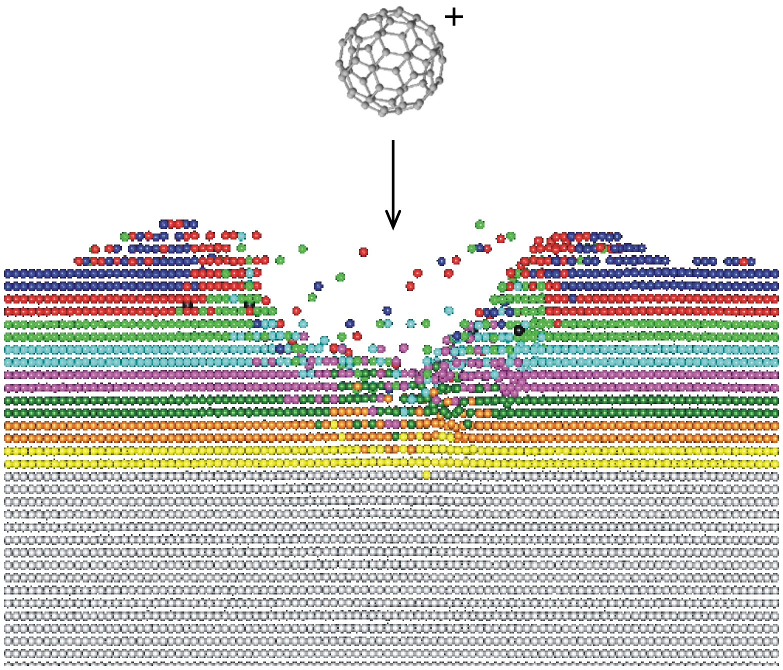
$\mathbf{Ar_n^+, C_{60}^+, SF_5^+, C_{24}H_{12}^+}$

Monomer vs Cluster damage

Ga at 15 keV



C_{60} at 15 keV



Microscopic insights into the sputtering of Ag{111} induced by C_{60} and Ga Bombardment, J. Phys. Chem. B, **108**, 7831-7838 (2004).

Effects of sputtering TiO_2

$$\mathbf{TiO_2} \longrightarrow \mathbf{TiO_x} \qquad x < 2$$

TiO_2 reduces to **Ti_2O_3** and **TiO**

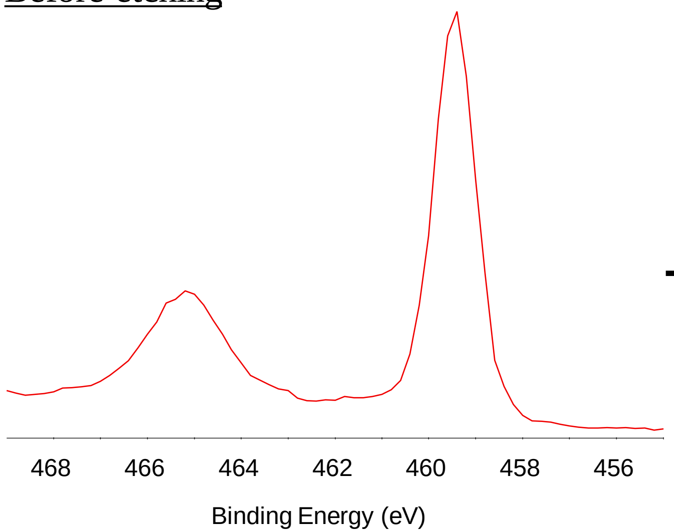
$\mathbf{TiO_2 \rightarrow Ti^{4+}}$ BE = 458.8 eV

$\mathbf{Ti_2O_3 \rightarrow Ti^{3+}}$ BE = 457.8 eV

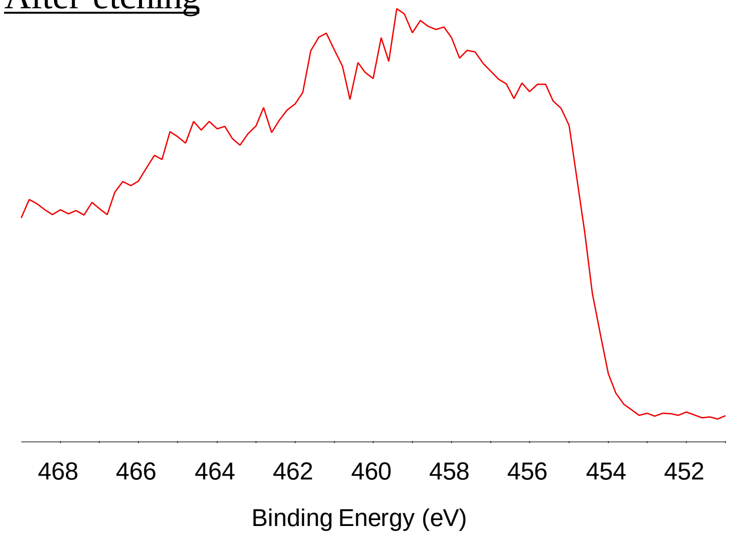
$\mathbf{TiO \rightarrow Ti^{2+}}$ BE = 455.6 eV

Ti 2p

<u>Before etching</u>



<u>After etching</u>

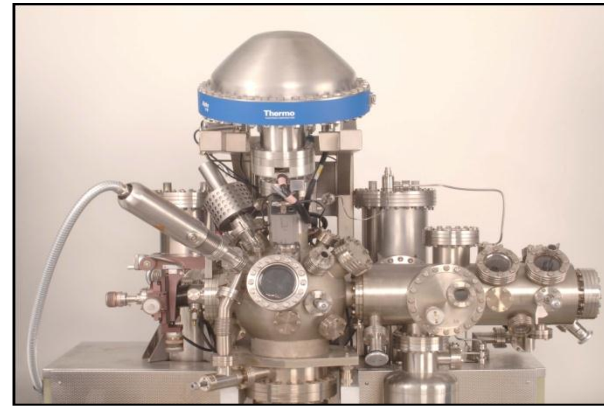


Bonding and quantitative information on the original film is lost

Experimental details

Theta Probe, by Thermo Scientific

K-Alpha, by Thermo Scientific



ESCALAB Mk II, by Thermo Scientific

1. Surface characterisation:

Source: Monocromated Al Kα, ($h\nu$=1486.6 eV)
140W, 400 μm spot
Pass energy: 300 eV for survey
50 eV for high resolution spectra

2. Etching at 3 kV and **3.** 200 V:

Source: Al Kα, ($h\nu$=1486.6 eV)
Ion gun: Ar^+ monomer

Etching 1

Voltage: 3 kV,
Beam current: 4 μA,
Raster size: 2 mm × 4 mm

Etching 2

Voltage: 200 V,
Beam current: 1 μA,
Raster size: 2 mm × 4 mm

4. Etching with 4 kV Ar_n^+ cluster source:

Source: Al Kα, ($h\nu$=1486.6 eV)
Ion gun: Ar_n^+ clusters (prototype)
Cluster size: ~ 1000 atoms

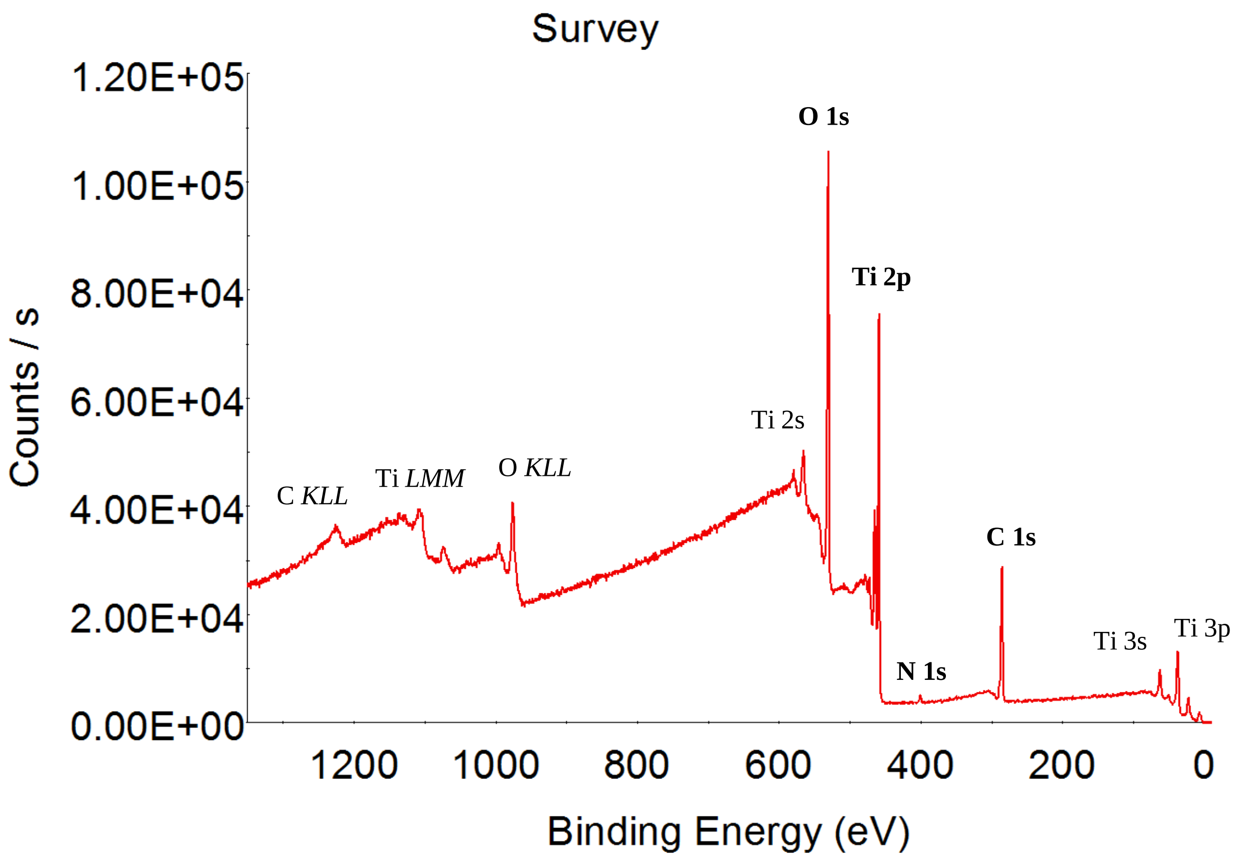
Etching 3

Voltage: 4 kV,
Beam current: 10 nA,
Raster size: 2 mm × 2 mm

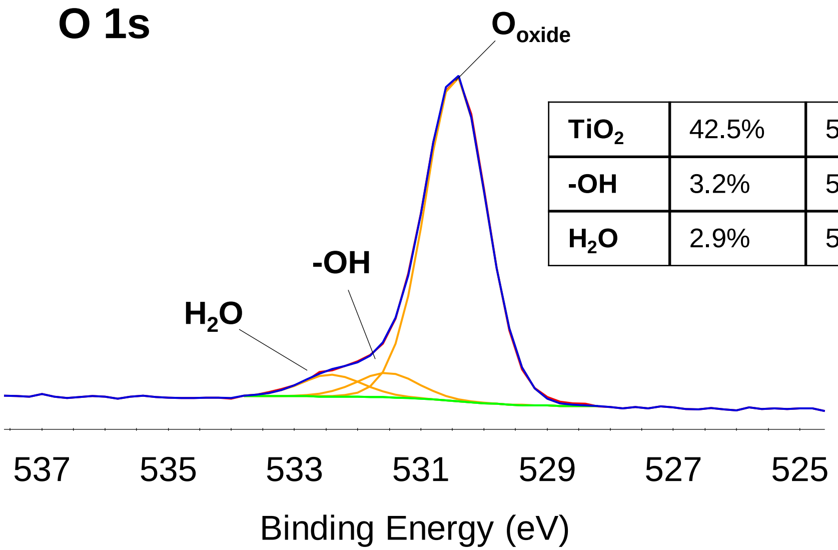
Adventitious C-H (C1s = 285.0 eV) was used as reference for charge shift correction
Avantage software (Thermo Scientific) used for data processing

XPS surface characterization

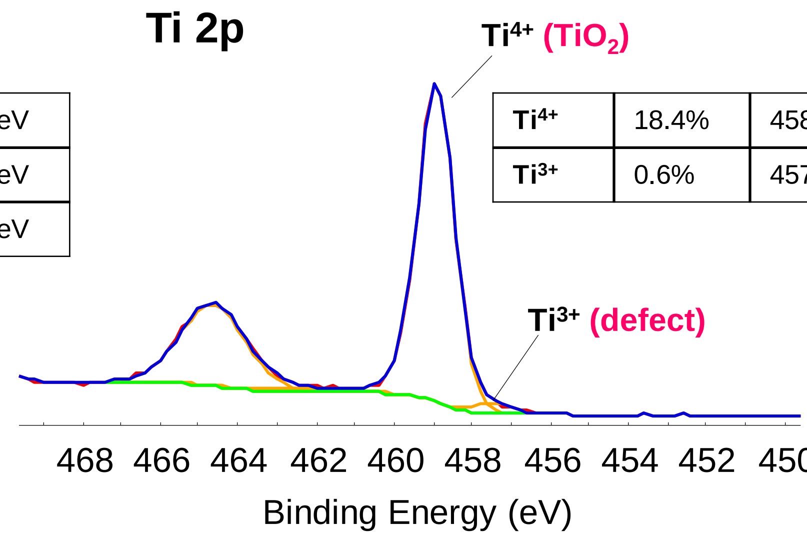
Specimen: Undoped nominal TiO_2 thin film deposited by reactive FVAD



Composition of the native TiO_2 film surface



TiO_2	42.5%	530.4 eV
-OH	3.2%	531.5 eV
H_2O	2.9%	532.4 eV

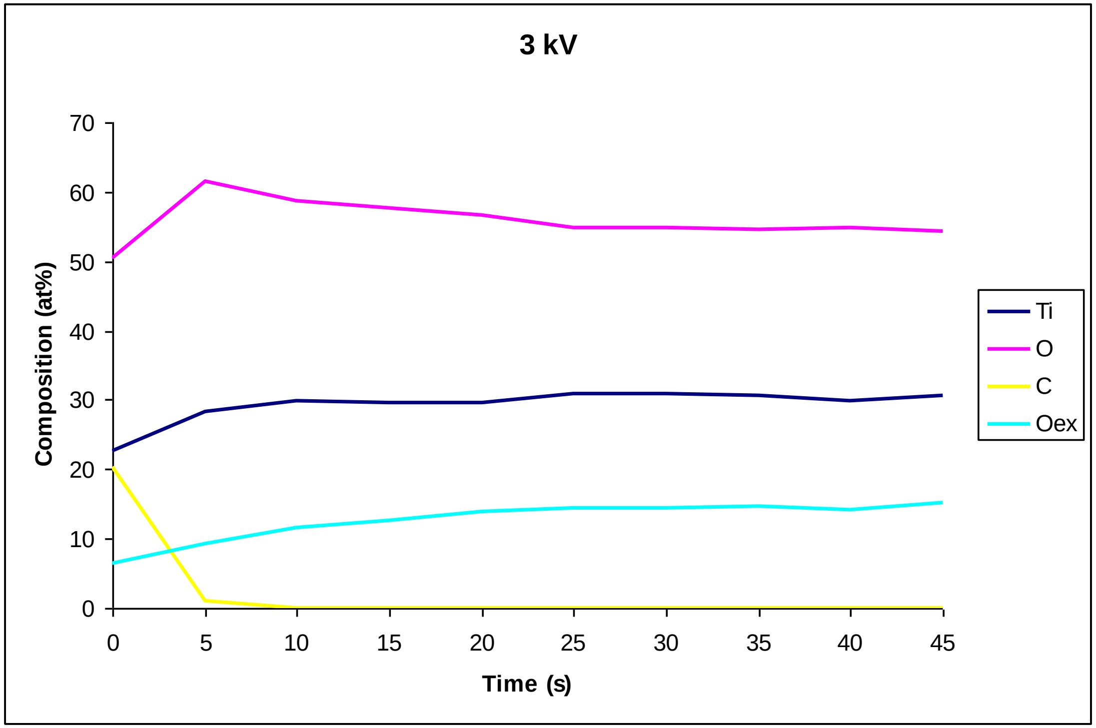


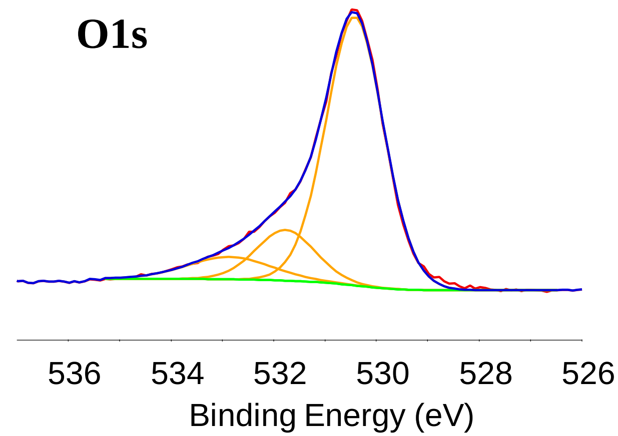
Ti^{4+}	18.4%	458.9 eV
Ti^{3+}	0.6%	457.4 eV

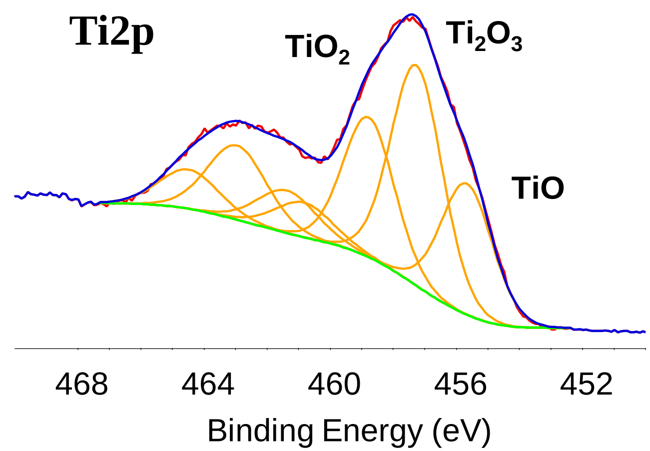
Composition (at%)

C1s	**Ti2p**	**N1s**	**O1s tot**	**O1s ox**	**O_{tot}/Ti**	**O_{ox}/Ti**
31.5	19.0	0.9	48.6	42.5	2.56	2.24

Etching results: Ar^+ ion beam, 3 kV







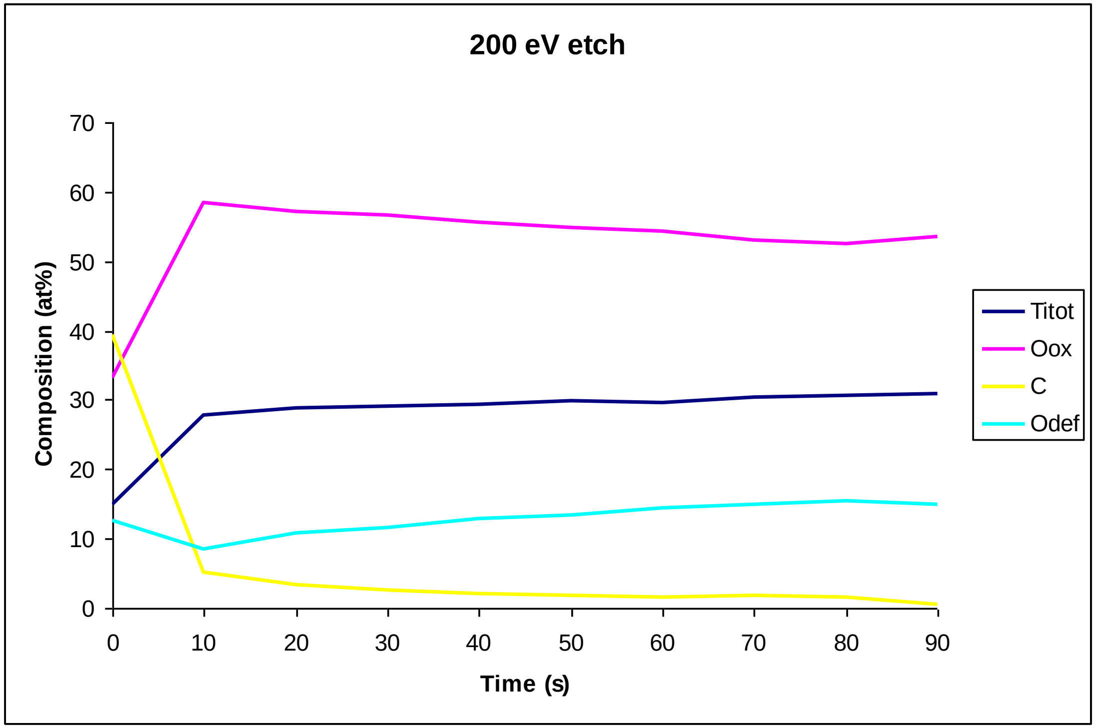
	C1s	Ti2p	O1s tot	O1s ox	O_{tot}/Ti	O_{ox}/Ti
Comp.(at%)	-	30.5	69.5	54.4	2.27	1.78

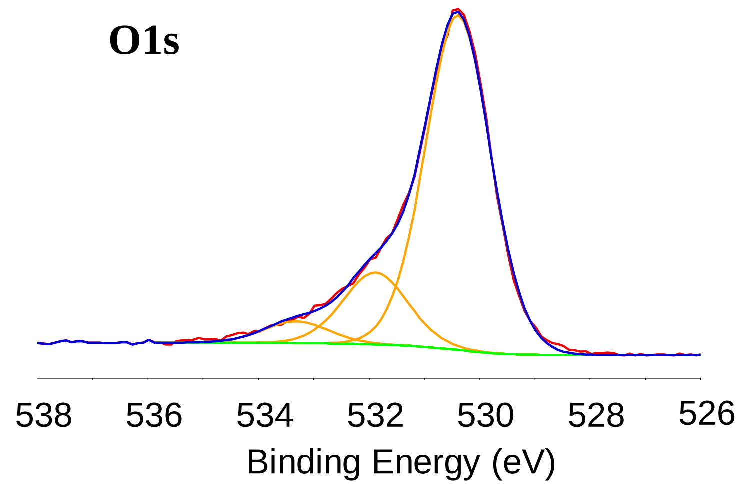
O_{oxide}	52.5%	530.4 eV
-OH	10.2%	531.9 eV
H_2O	6.4%	533.3 eV

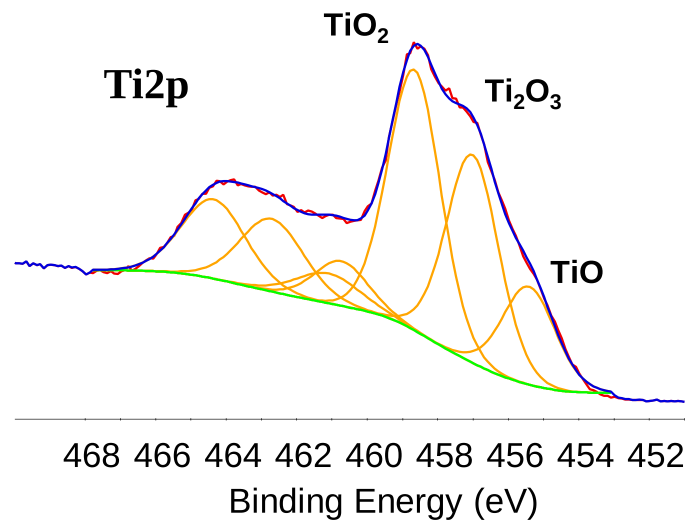
Ti^{4+}	9.7%	458.8 eV
Ti^{3+}	13.2%	457.3 eV
Ti^{2+}	7.8%	455.7 eV

Charge shift correction: no

Etching results: Ar^+ ion beam, 200 V







	C1s	Ti2p	O1s tot	O1s ox	O_{tot}/Ti	O_{ox}/Ti
Comp.(at%)	0.5	30.8	68.7	53.6	2.23	1.74

O_{oxide}	53.5%	530.4 eV
-OH	11.6%	531.9 eV
H_2O	3.5%	533.3 eV

Ti^{4+}	14.6%	458.7 eV
Ti^{3+}	10.7%	457.0 eV
Ti^{2+}	4.9%	455.4 eV

Charge shift correction: no

Etching results: Ar^+ cluster source

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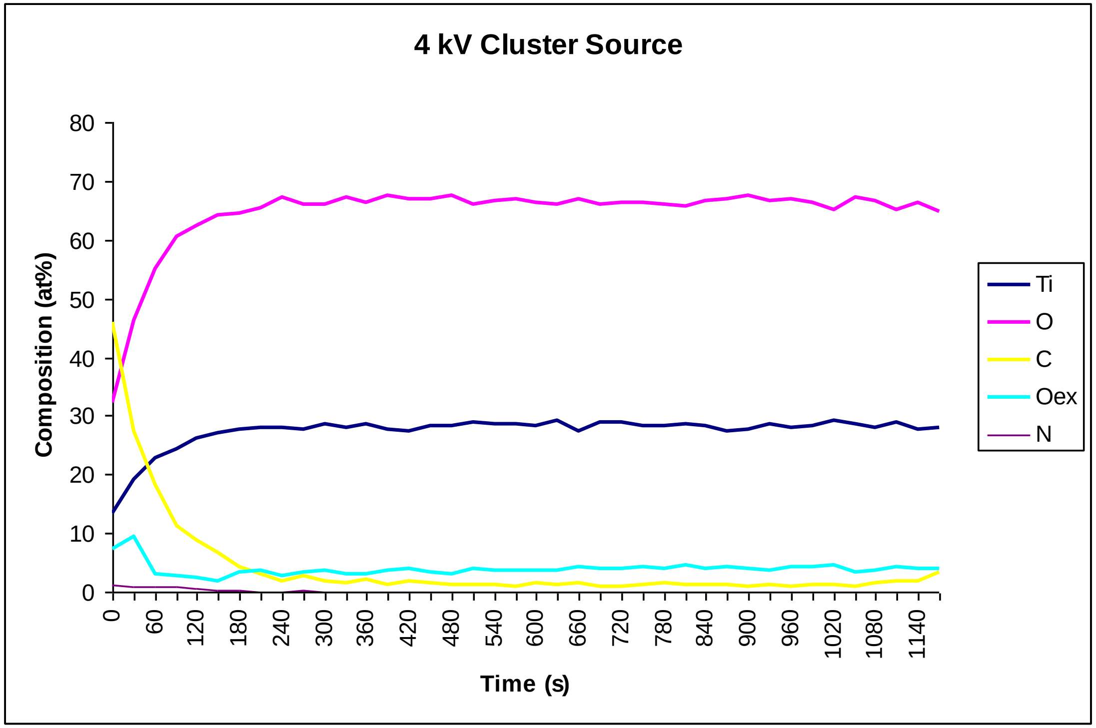

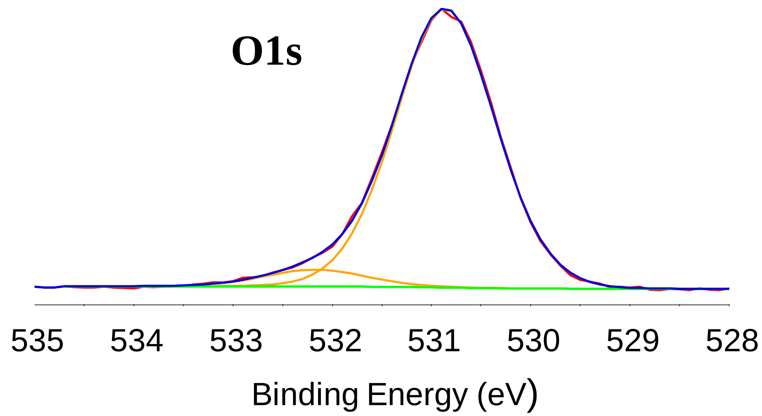

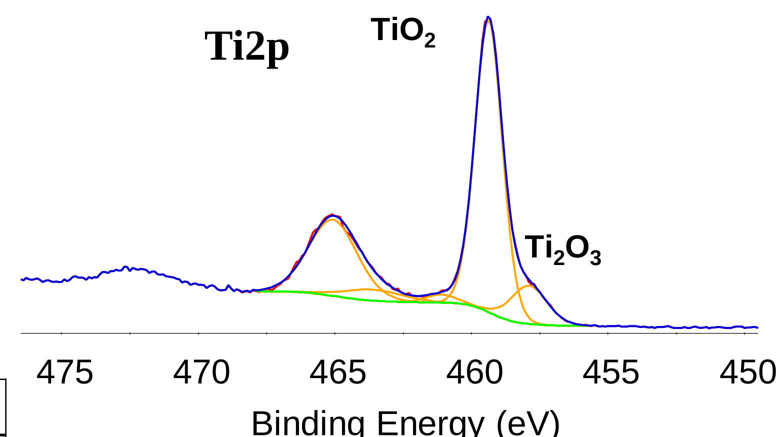

	C1s	Ti2p	O1s tot	O1s ox	O_{tot}/Ti	O_{ox}/Ti
Comp.(at%)	3.4	27.9	68.7	64.8	2.46	2.32

O_{oxide}	64.5%	531.0 eV
-OH	3.9%	532.4 eV

Ti^{4+}	24.4%	459.5 eV
Ti^{3+}	3.14%	457.8 eV

Charge shift correction: yes

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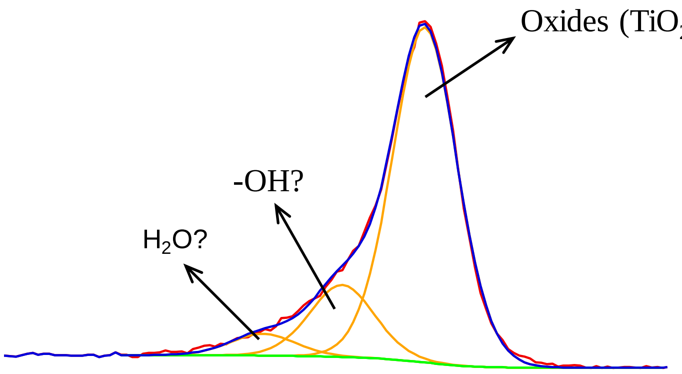
Oxygen peak interpretation

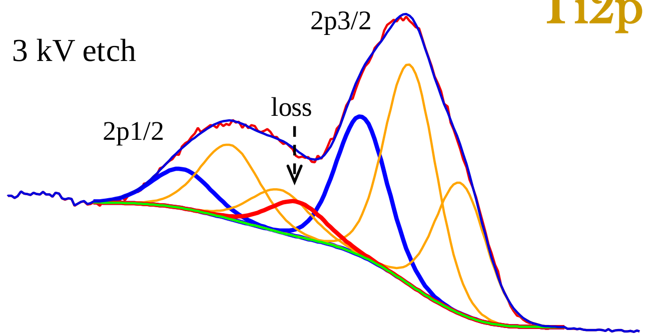


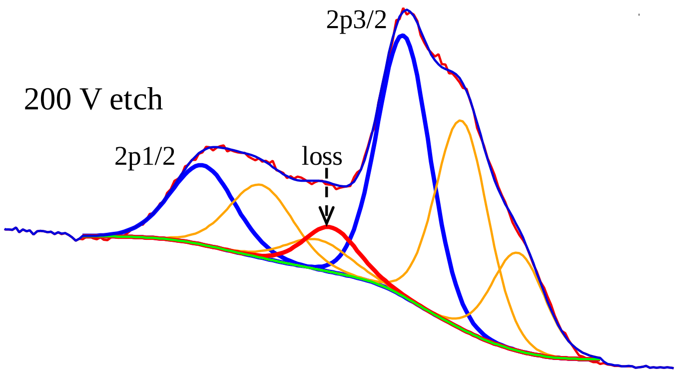
Surface hydroxyl groups and adsorbed water should be only on the surface, but the peaks at higher BE increase with etch time.

Possible interpretations from literature:

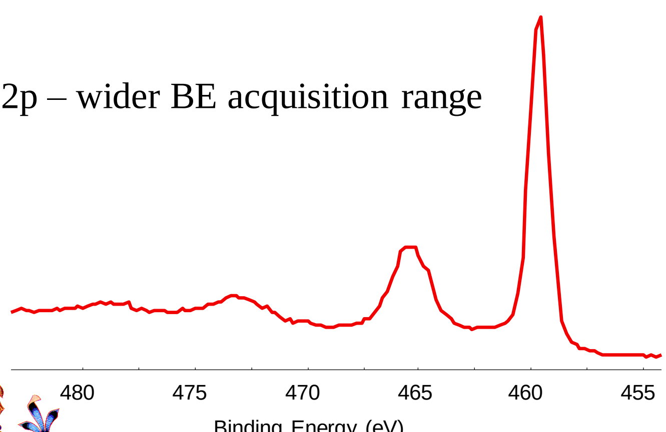
1. Back-deposition of oxygen on the surface
2. After reduction of Ti^{4+} to Ti^{3+} and Ti^{2+} the excess O diffuses from the bulk towards the surface and forms OH groups
3. Free electrons in the film may become localized at Ti sites, forming Ti^{3+} and increasing the Ti-O bond length, because of partial filling of anti-bonding orbitals. This may increase the BE of O1s electrons.
4. Formation of ‘defective’ oxygen sites: highly polarized oxygen atoms near to oxygen vacancies (z = +2) or tri/tetravalent Ti interstitials (z = +3, +4)
5. Oxygen atoms with a lower electron density, described as O^-, this happens when the co-ordination number is less than 3 (less than 3 Ti atoms bonded to one O), giving M-O bonds with a higher covalent nature. The atoms may re-arrange to this configuration after formation of a Ti vacancy.

Ti2p quantification issues

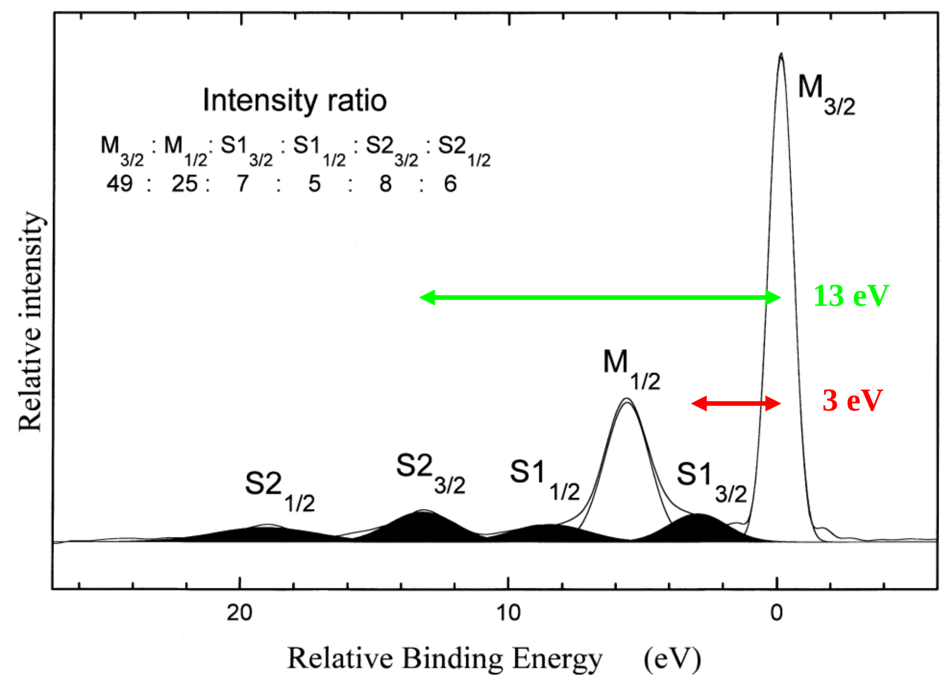




Ti 2p – wider BE acquisition range

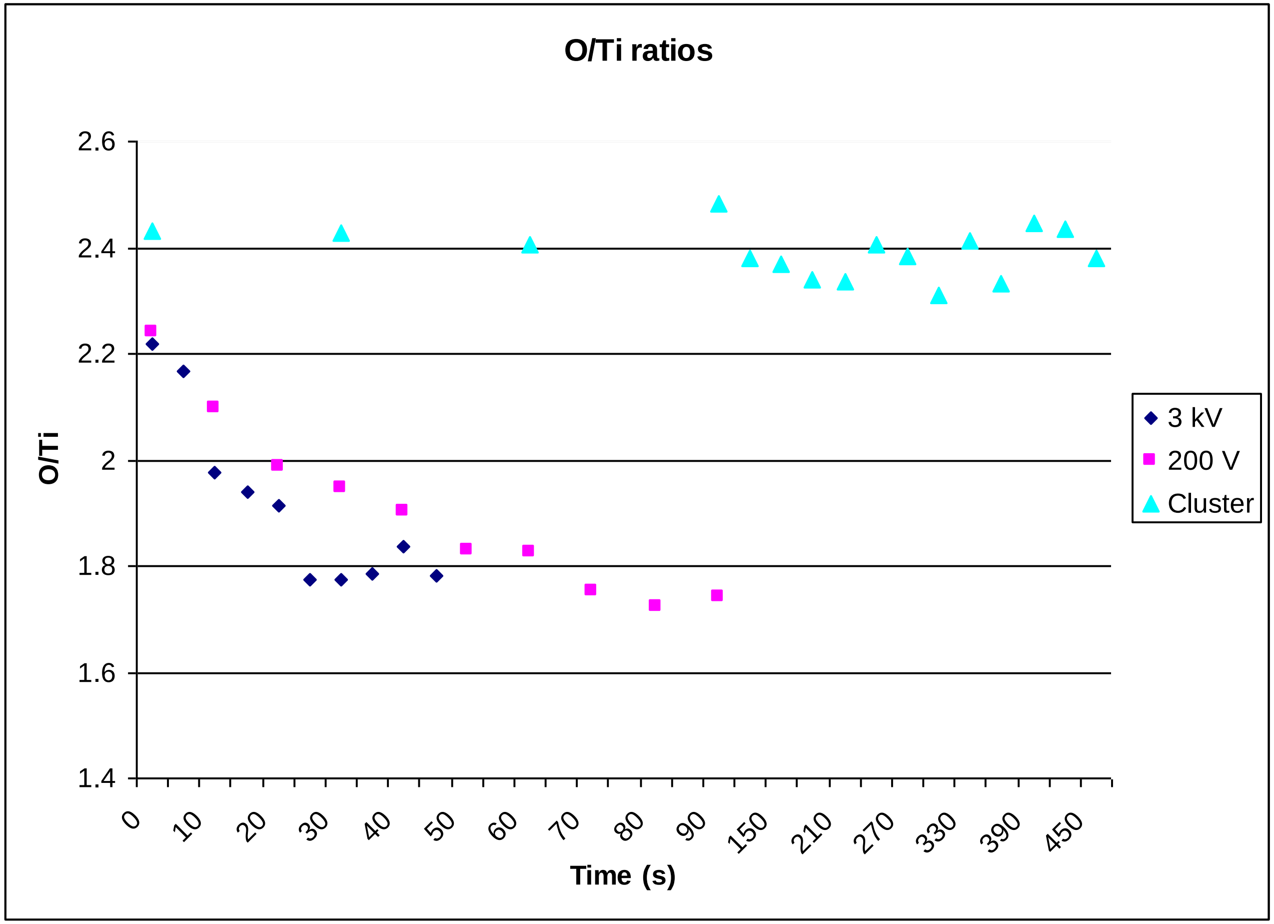


Quantification of TiO_2 always shows an excess of oxygen



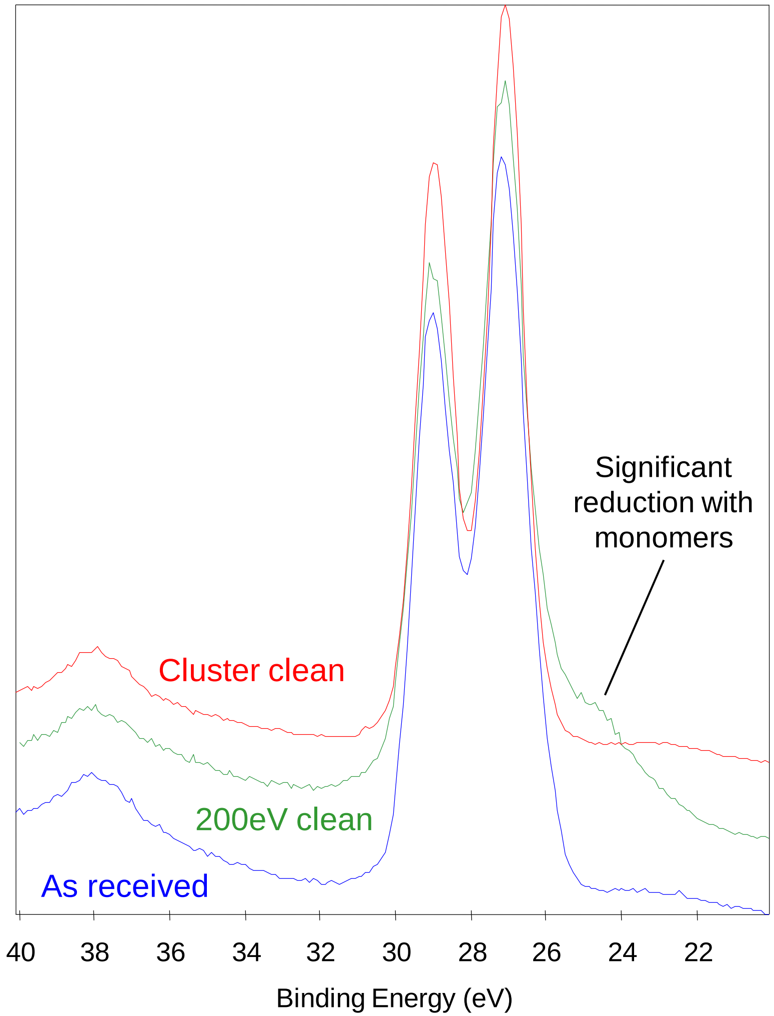
M.Oku et al. *Journal of Electron Spectroscopy and Related Phenomena*, 105 (1999) 211-218

O/Ti ratio after sputtering for the different ion beam conditions



- Tantalum oxide film (Ta_2O_5)
  - Even low energy monomer cleaning causes a significant amount of reduction
  - Argon cluster cleaning gives no visible sign of oxide reduction
  - Quantification after argon cluster cleaning confirms Ta_2O_5 stoichiometry ($\pm$ 1 at%)

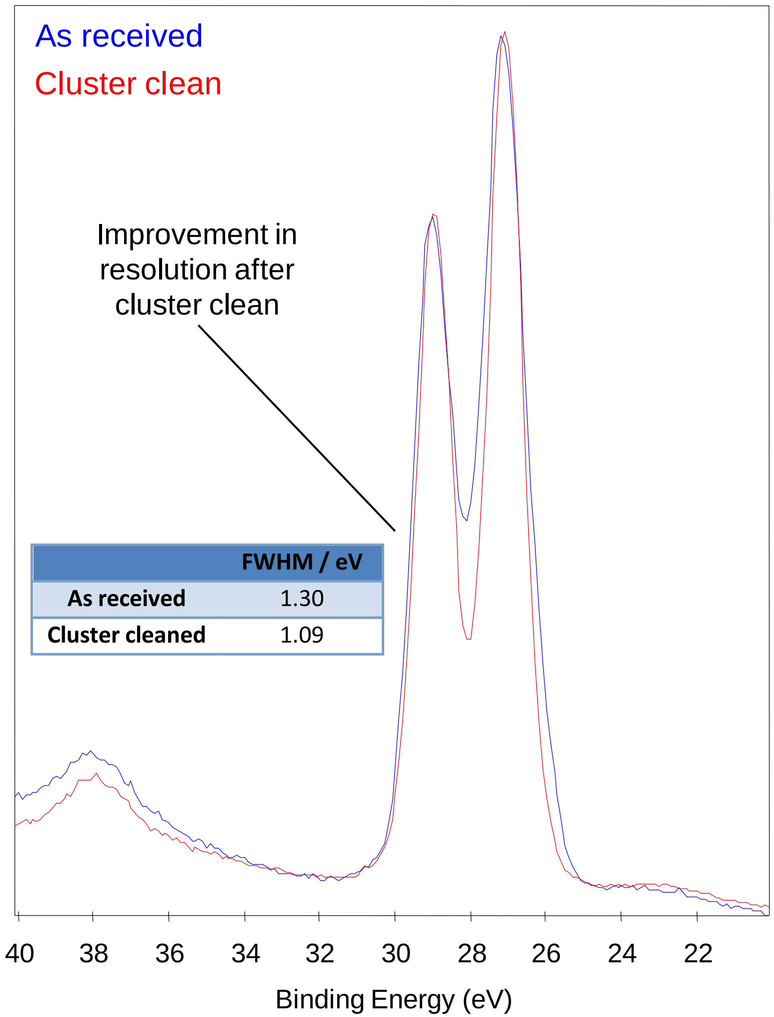
Clean method	Ta4f oxide	Ta4f reduced
None	100	-
Cluster	100	-
200eV monomer	70.4	29.6



Benefits of cluster cleaning (Ta_2O_5)

In addition to reduced preferential sputtering:

- Increased photoelectron signal
  - Removal of attenuating contamination
- Apparent improvement in energy resolution observed in Ta 4f region
  - Removal of other Ta compounds (hydroxides, carbonates, etc)



	FWHM / eV
As received	1.30
Cluster cleaned	1.09

Conclusions

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- Preferential sputtering of TiO_2 (and Ta_2O_5) are substantially reduced using an Ar_n^+ cluster source.
- The effect of ion beam etching TiO_2 leads not only to preferential sputtering of O, but also a modification of the bonding or polarization of O atoms in the TiO_2 bulk structure.
- The normal quantification of TiO_2 using the Ti 2p envelope leads to an under estimation of the Ti atomic percentage, as loss peaks have to be taken into account.
- The use of Ar_n^+ cluster sources has the potential to resolve (or substantially improve) XPS preferential sputtering problems for many important technological functional materials and thin films (oxides, chalcogenides etc,) – hence, providing accurate composition information.

Acknowledgements: Thanks to Prof. Ray Boxman, Tel Aviv University, Israel, for providing the TiO_2 thin films.