Preparation of ordered Mo+Ti and V+Ti mixed oxide layers on TiO_2(110) using a W+Ti oxide diffusion blocking layer

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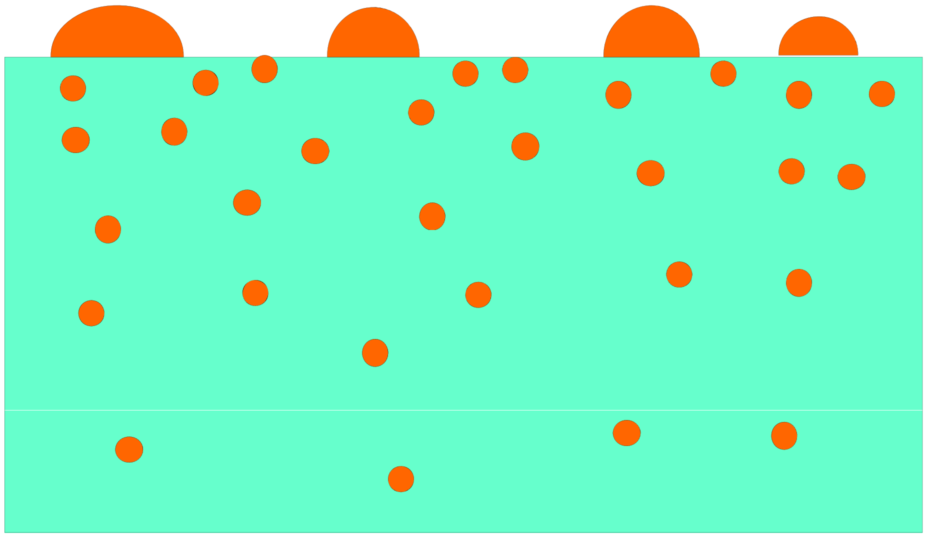
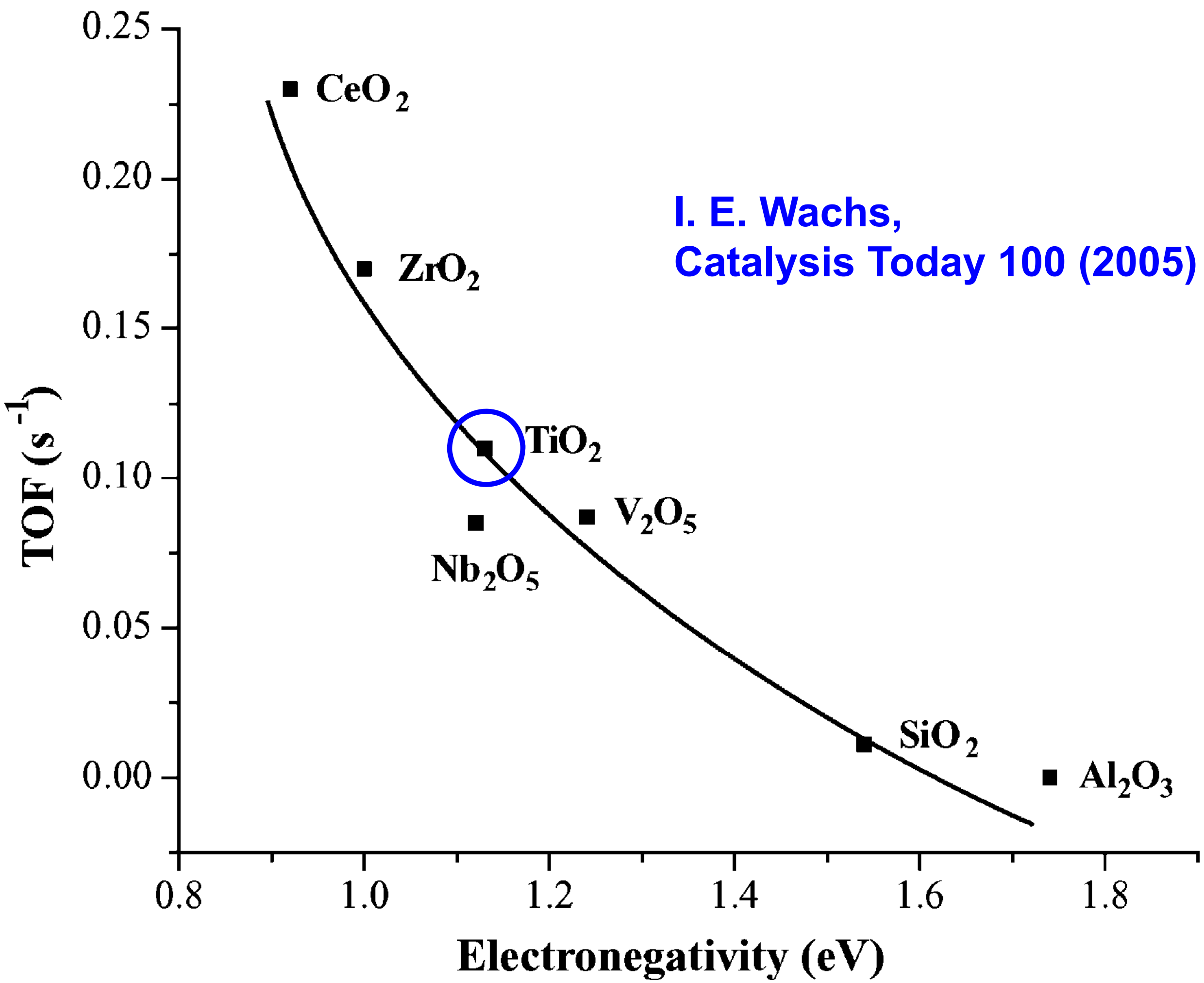
- Supported catalyst with part of the active component in the support.
- Mixed oxide with phase separation.



- Chemical activity of the mixed phase?
- What phases are to be expected?
- How are the atoms of the active component embedded into the substrate lattice?
- How does the matrix modify the chemical properties of the embedded atoms?
- Oxidation states?
- Equilibrium between surface and bulk component?
- Influence of gases (oxygen!)?
- How to prepare?



I. E. Wachs,
Catalysis Today 100 (2005) 79–94

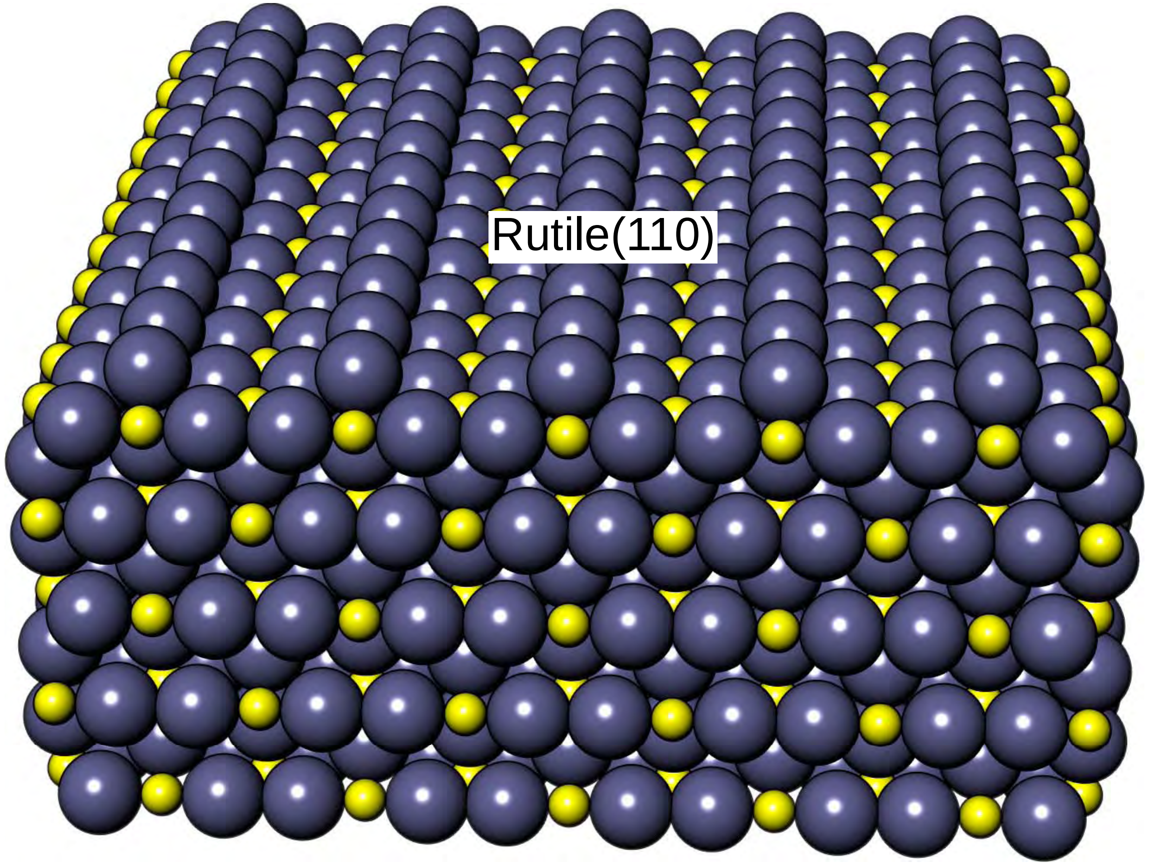
Preparation strategies

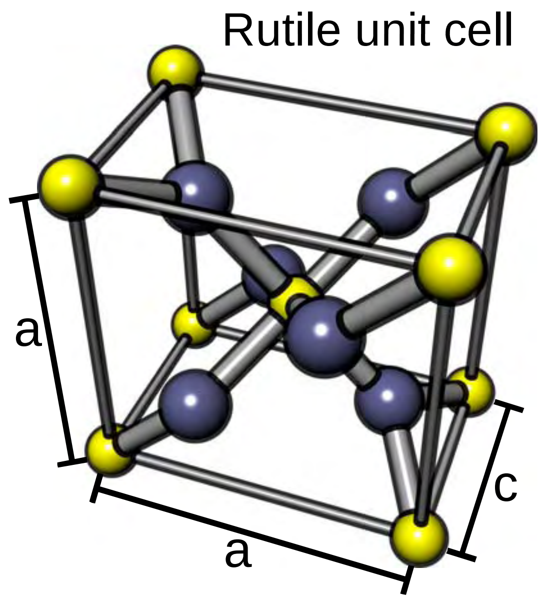
- **Deposition of metal onto support followed by annealing.**
- **Direct preparation of a mixed oxide.**

Interested in the properties of the mixed phase ➔ direct preparation.

- ➢ **Better control of composition.**

- **Co-deposition of two metals in an oxygen atmosphere.**
- **Concentration of the mixed-in metal: not too high.**
- **Systems: TiO_2 mixed with Mo and V.**



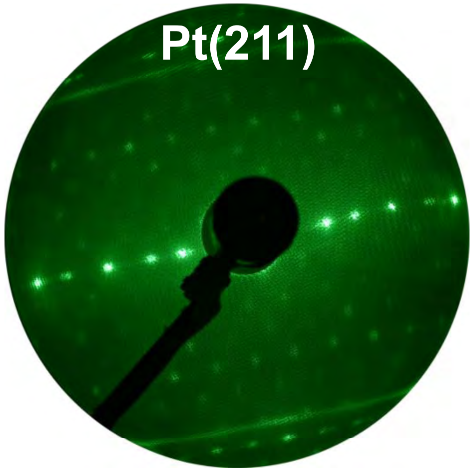


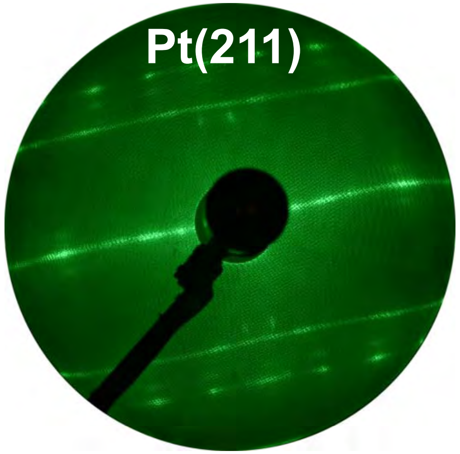
MoO_2 and VO_2 both exhibit rutile structure: good mixing with TiO_2. Other oxidation states have a tendency for phase separation.

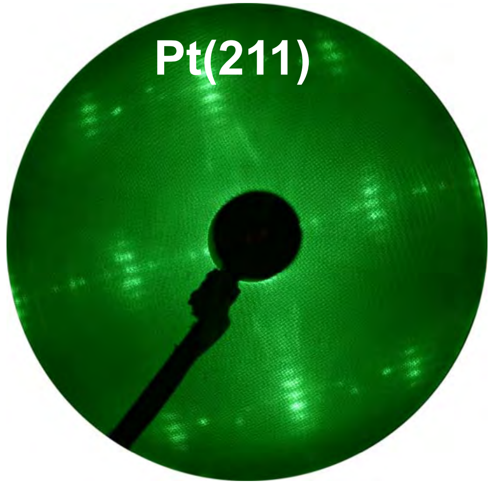
Lattice parameter for different rutile-type oxides

oxide	a	c
CrO_2	4.41	2.91
MoO_2	4.86	2.79
RuO_2	4.51	3.11
SnO_2	4.74	3.19
TiO_2	4.59	2.96
VO_2	4.55	2.85
WO_2	4.86	2.77

TiO_2 preparation investigated on several Au and Pt surfaces. Thin layers: strange structures; thicker layers: dewetting, faceting, one-dimensional disorder. Probable problem: lattice mismatch







Preparation strategy -2-

To improve lattice match: use TiO_2(110) substrate

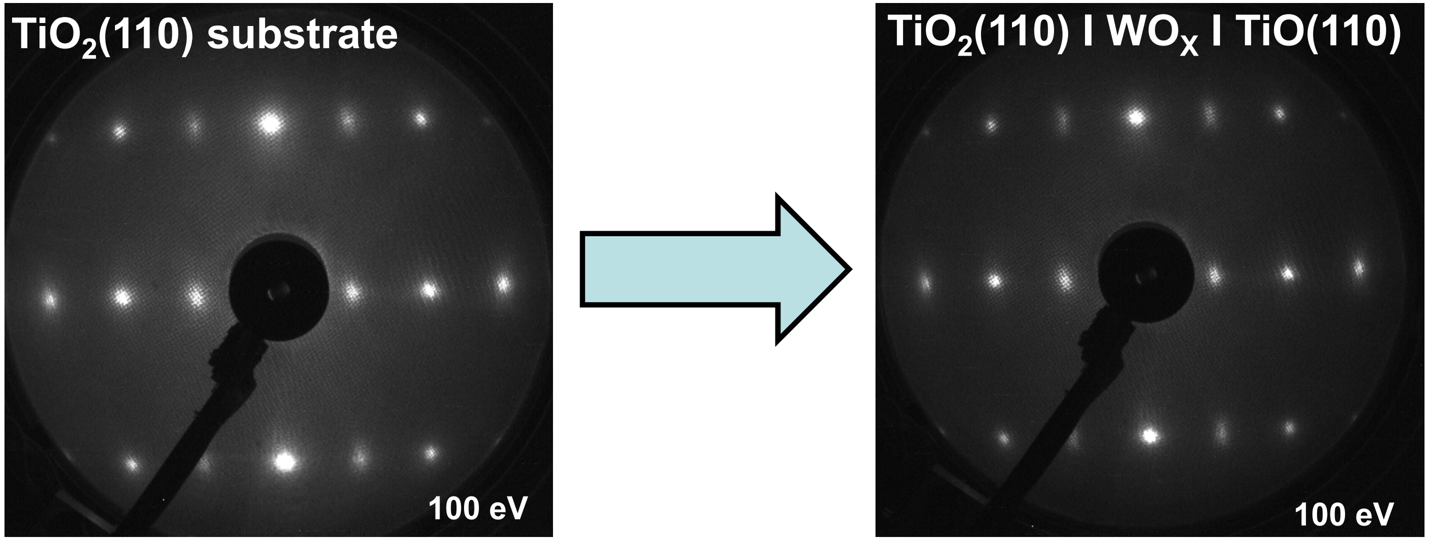
- **High-quality TiO_2(110) layers**

Stable layers of Mo in TiO_2(110).

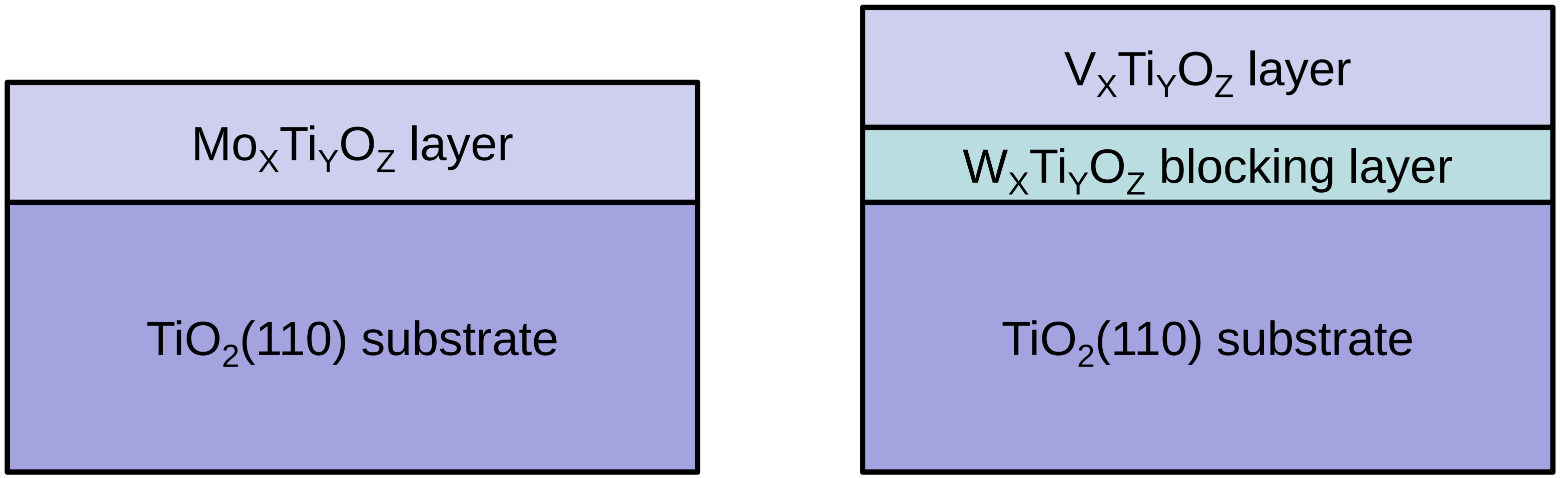
Problem: vanadium diffuses into the bulk.

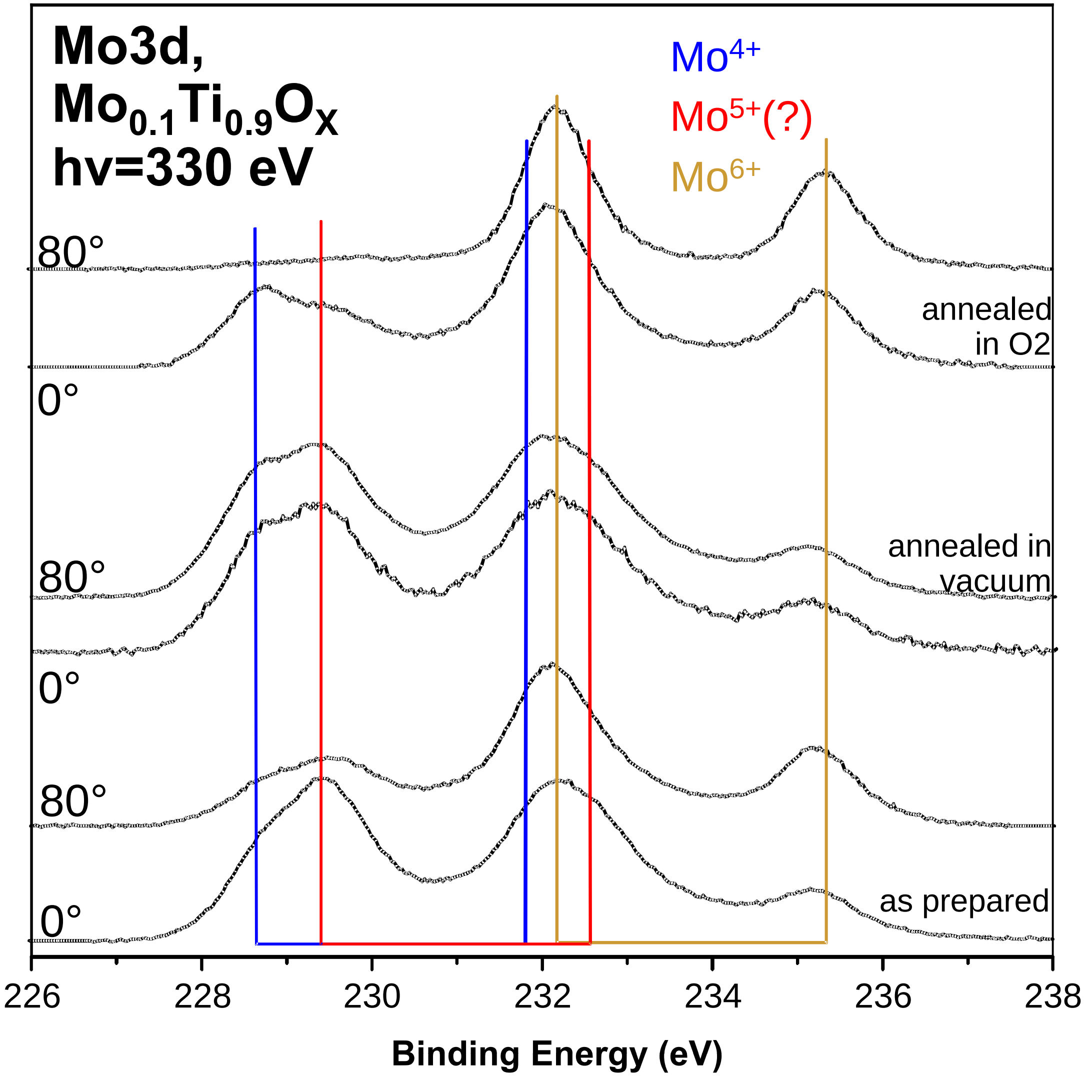
- **Prepare a diffusion blocking layer: (Ti+W)O_X**

Good quality of TiO_2(110) on the blocking layer



Short summary - the systems are:



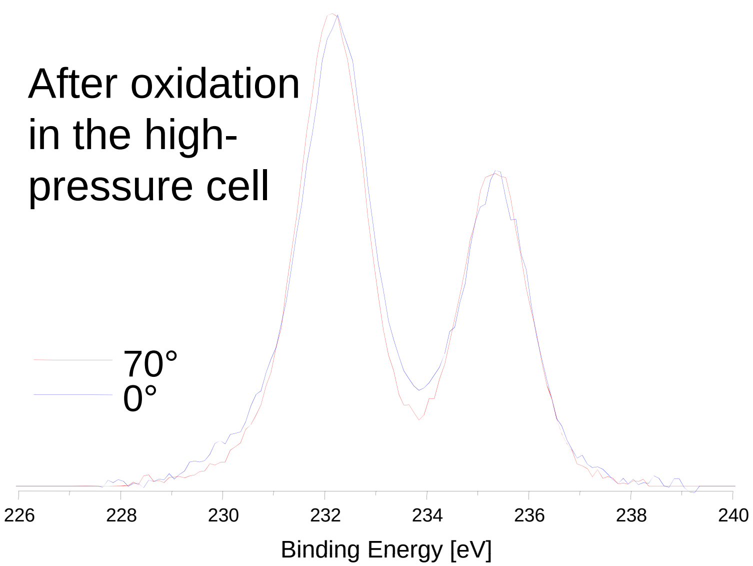


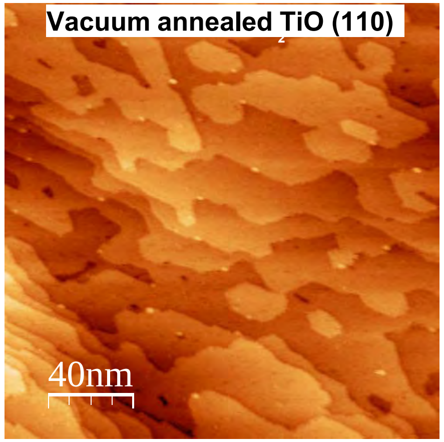
$Mo_XTi_YO_X$

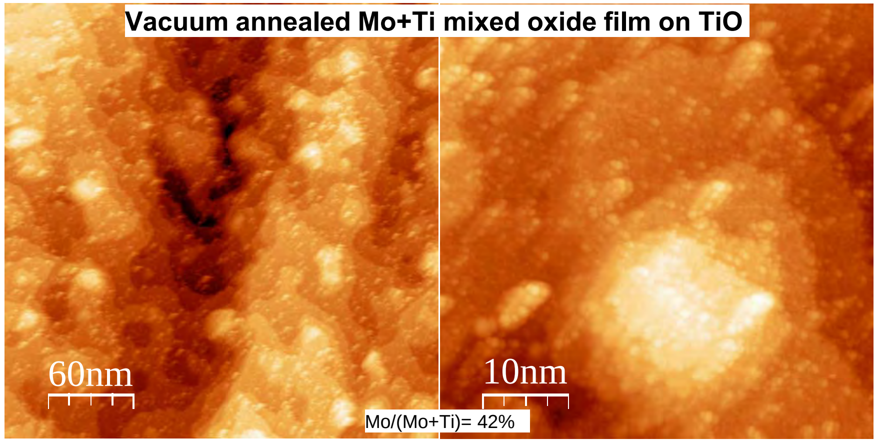
Oxygen treatment produces Mo^{6+} at the surface.

In the bulk: Mo^{4+}.

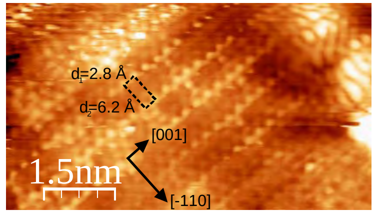
Part of the Mo^{6+} and Mo^{5+} possibly also in the bulk.

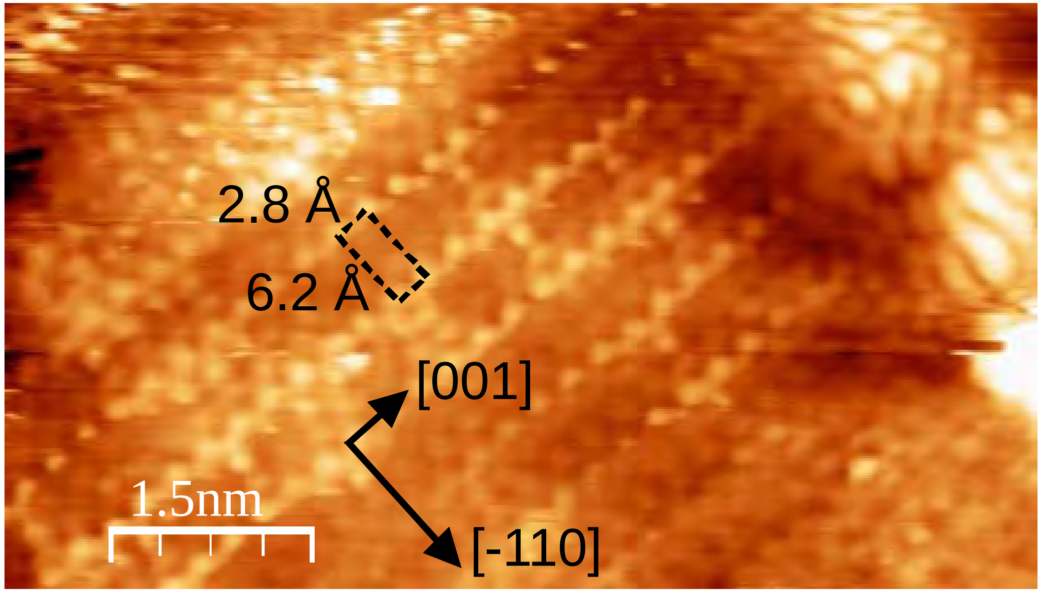




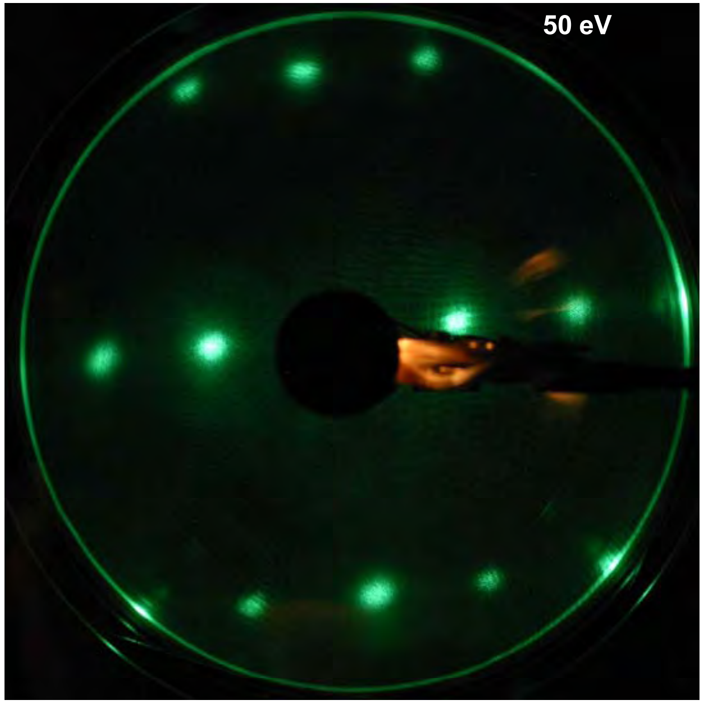


Vacuum annealed Mo+Ti mixed oxide

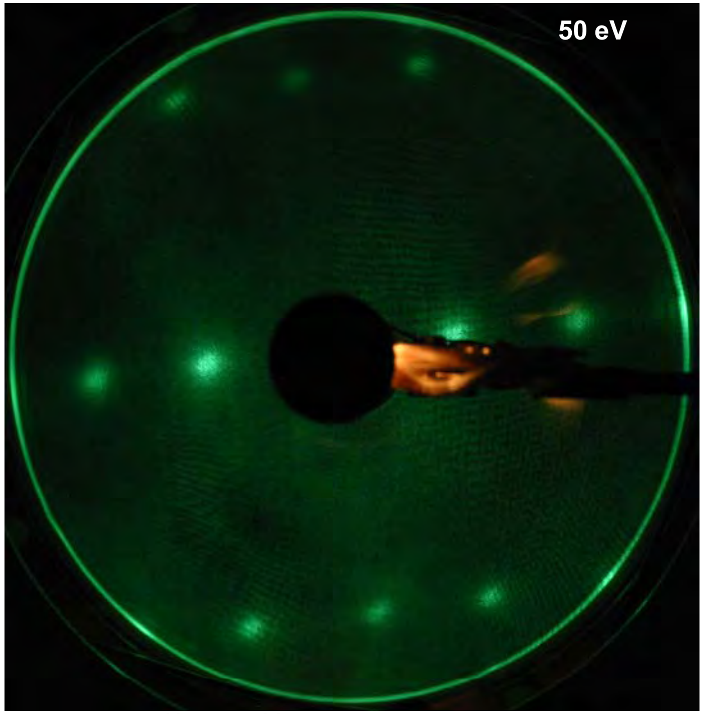




Protrusions on the surface are probably due to MoO_3.



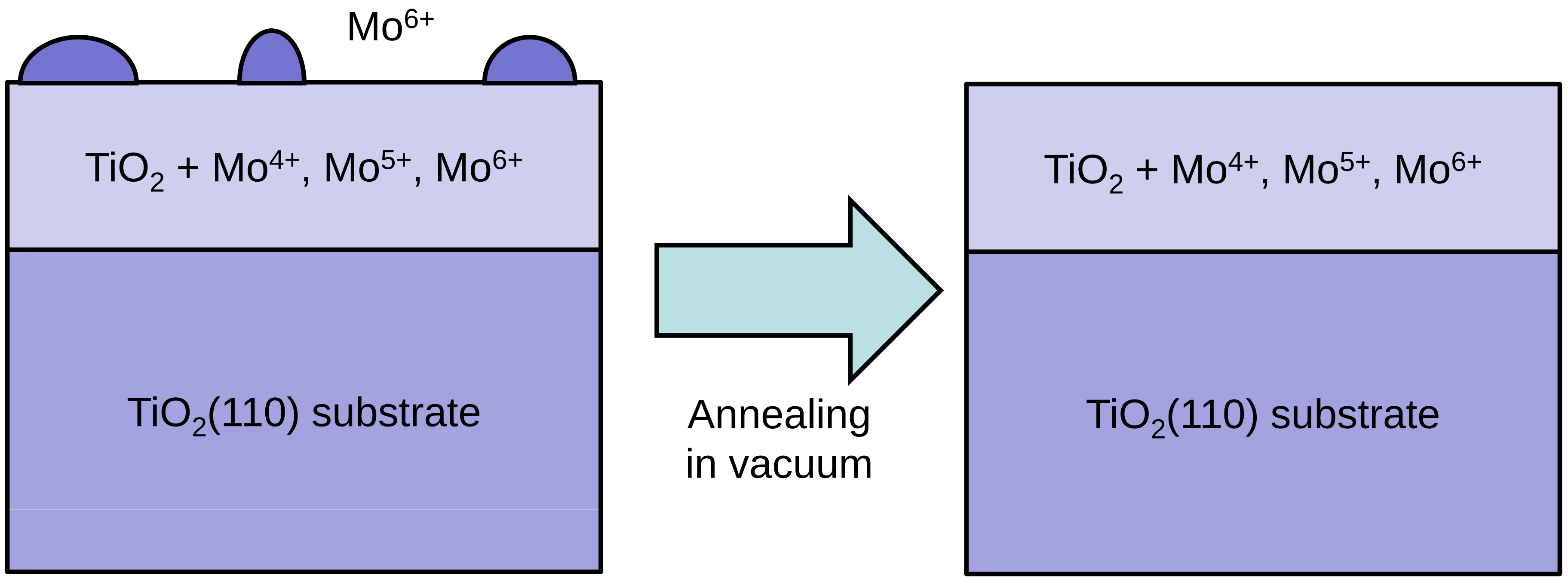
Mo/(Mo+Ti) = 2%



Mo/(Mo+Ti) = 38%

LEED pattern resembles TiO_2(110) pattern.

Short summary - $Mo_XTi_YO_X$



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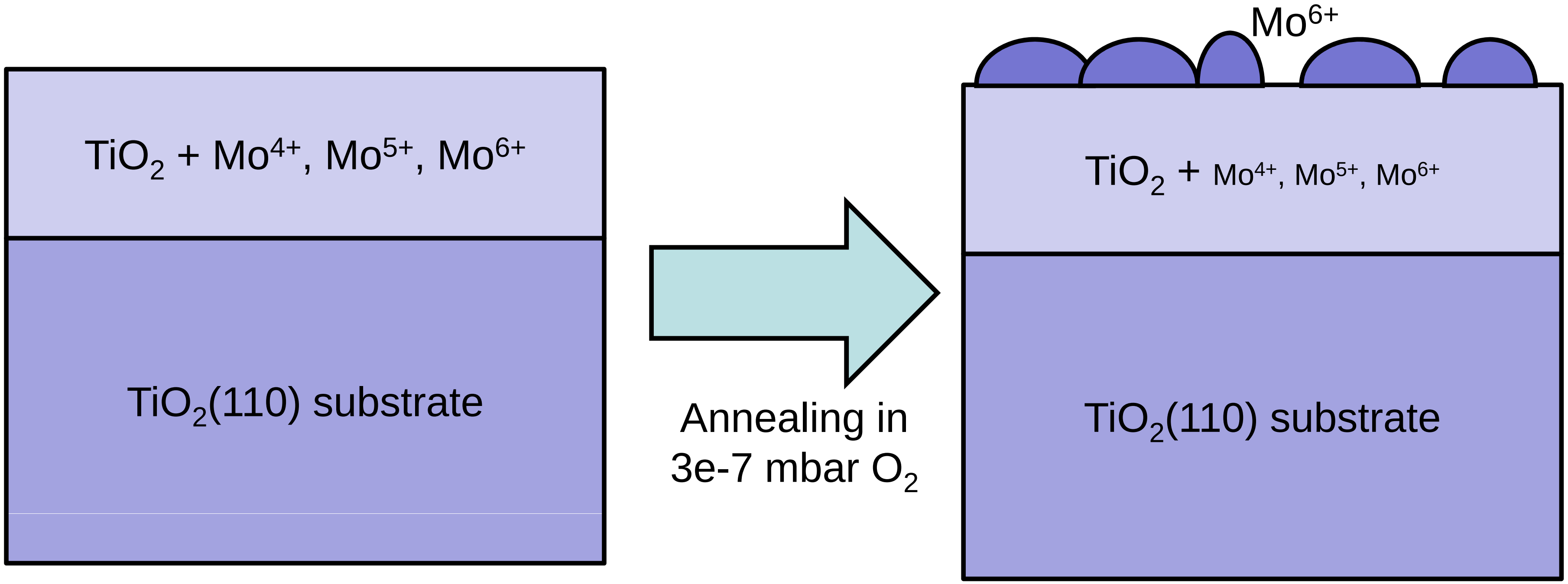

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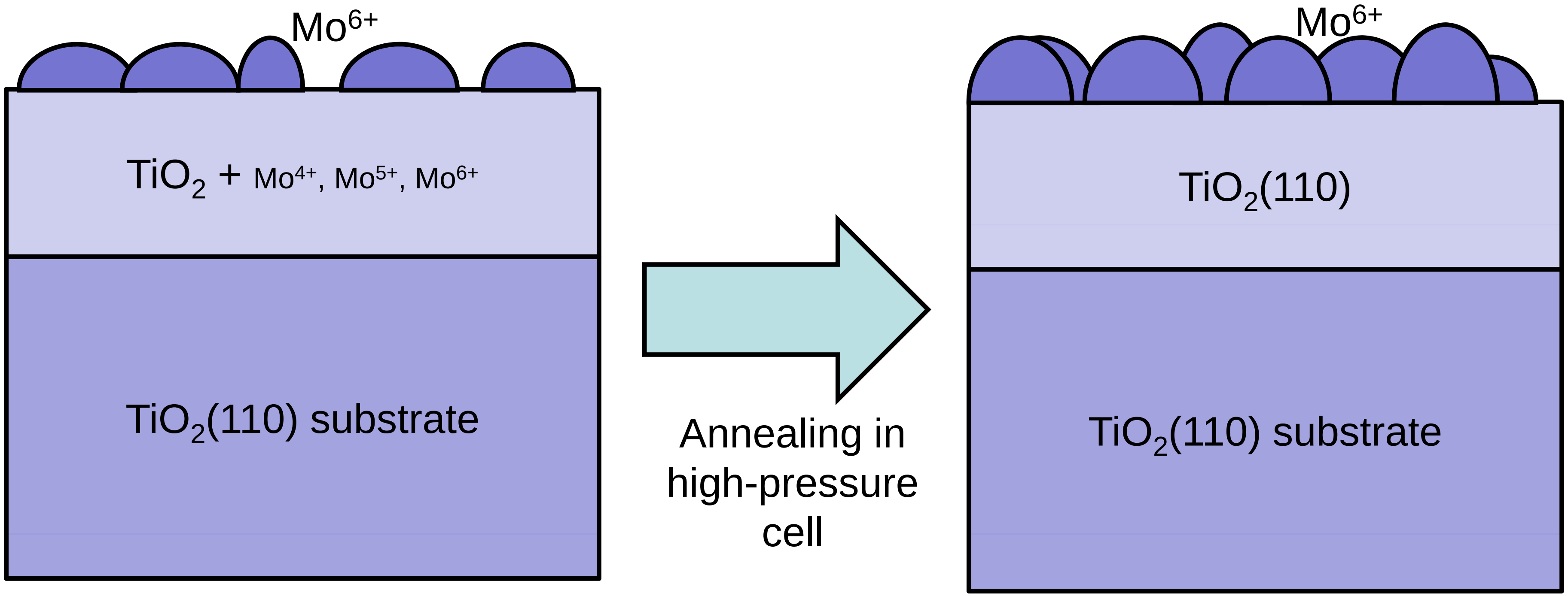
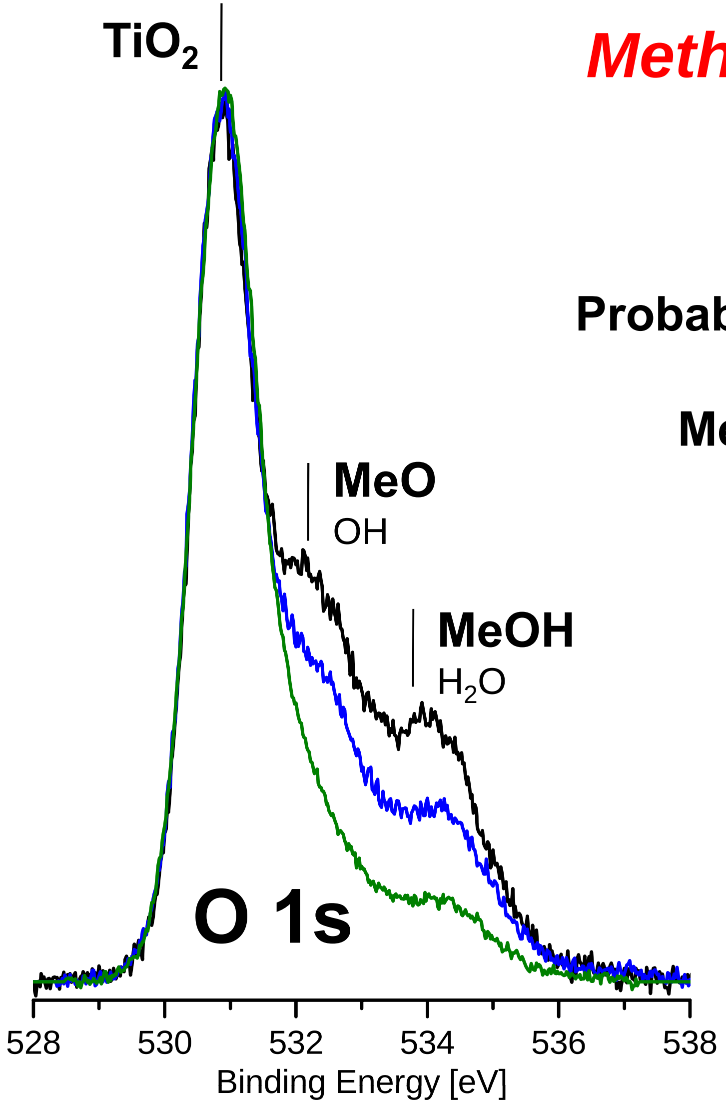
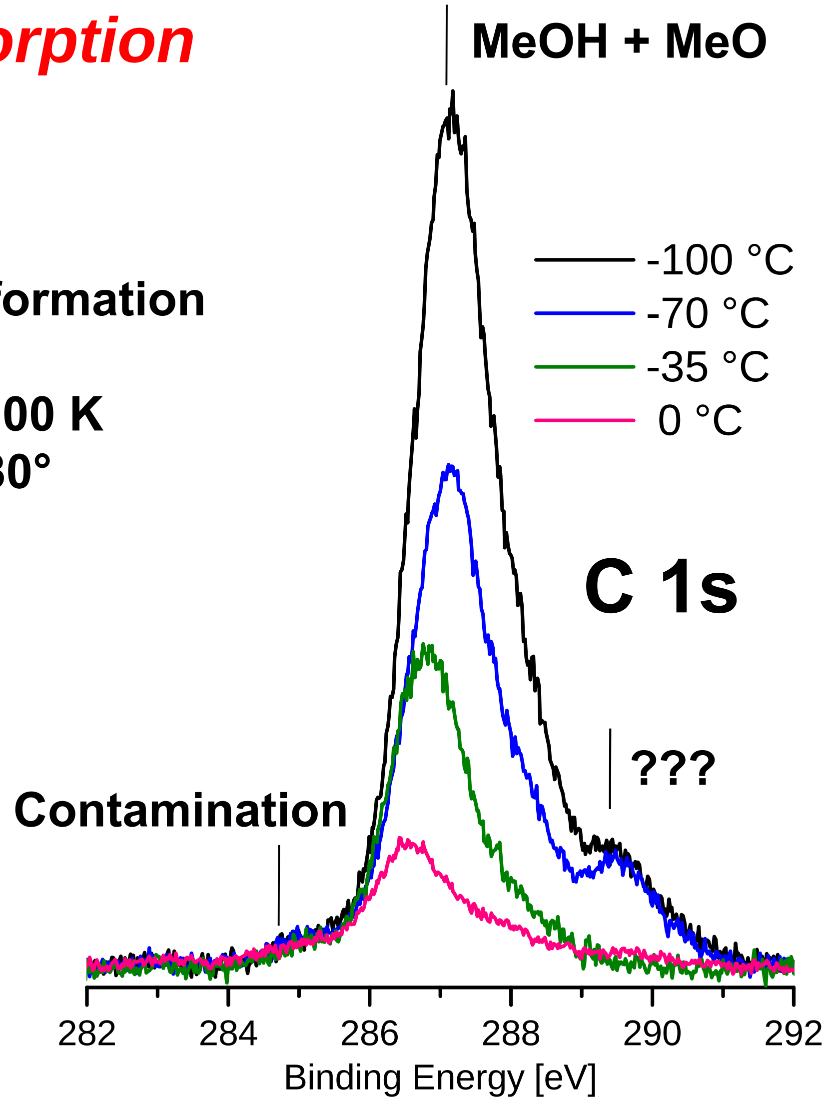


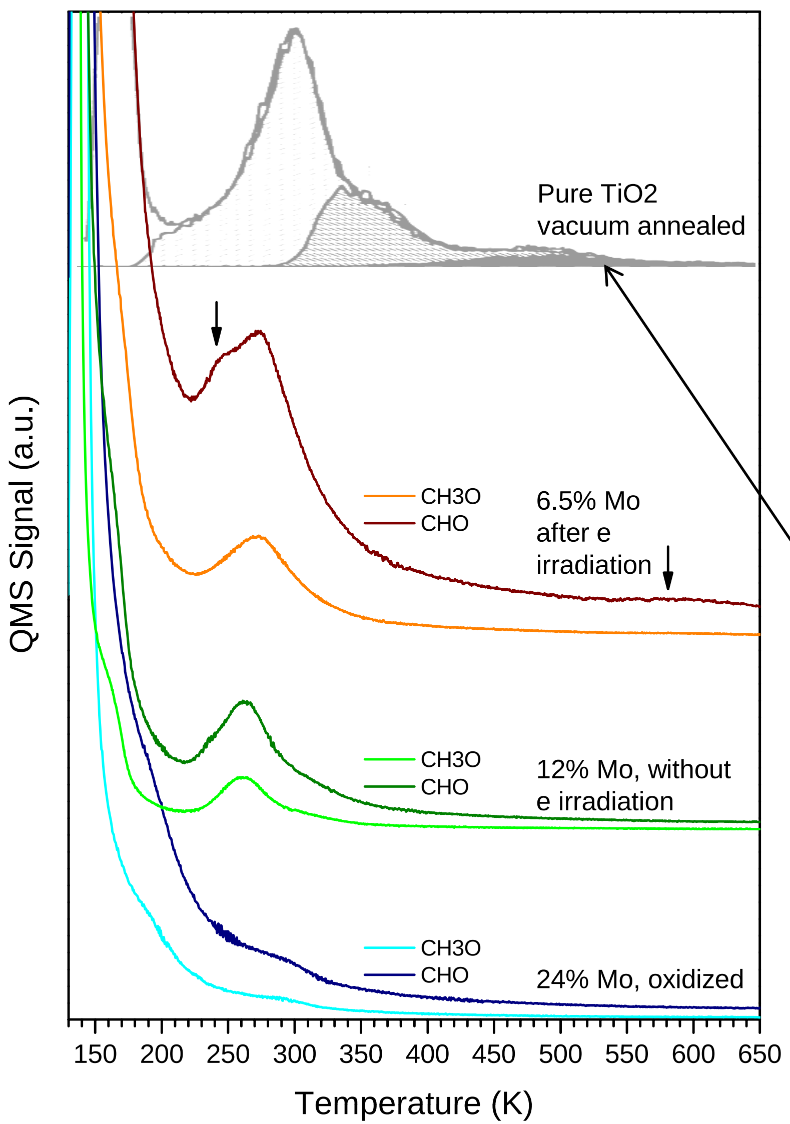
Methanol adsorption (XPS)



Probably methoxy formation

MeOH ads. at 100 K
Analyzer at 80°





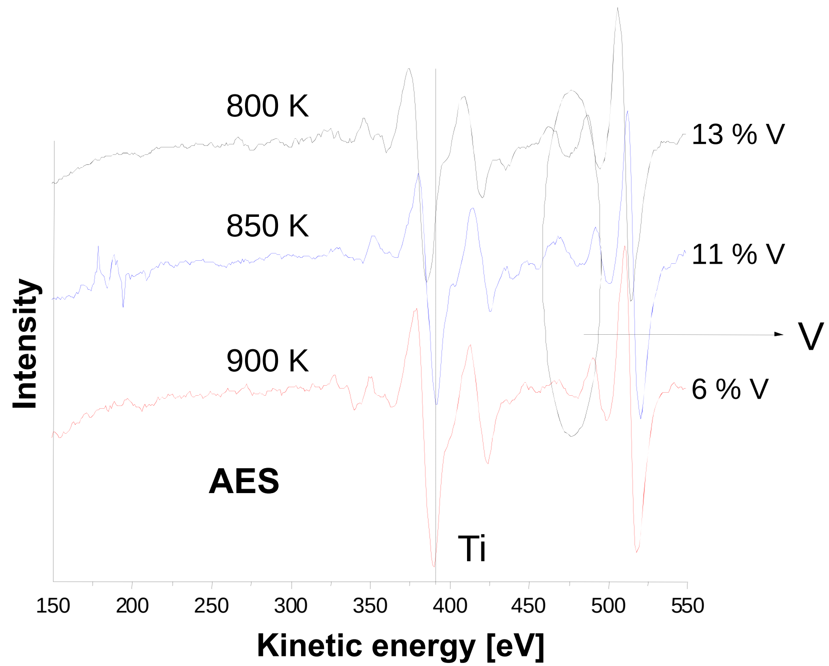
Methanol adsorption (TDS)

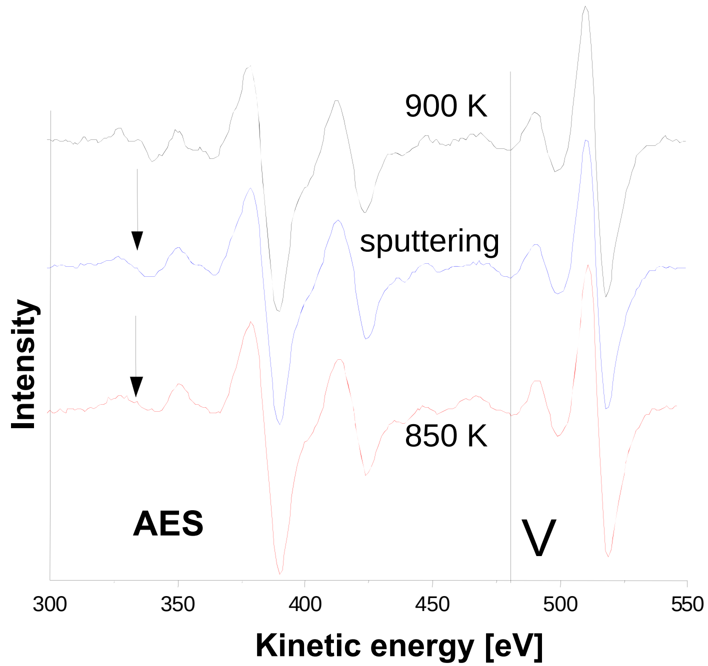
- Damping of the ~270K peak with increased Mo content.
- Large part of the signal due to TiO_2(110).
- Electron irradiated surface gives a formaldehyde peak.

Henderson et al., *Surf. Sci.*, 1998, 412/413, pp 252–272

Thermal stability of the V+Ti mixed oxide layer

$V_XTi_YO_Z$ | TiO_2(110) | WO_X | TiO_2(110)





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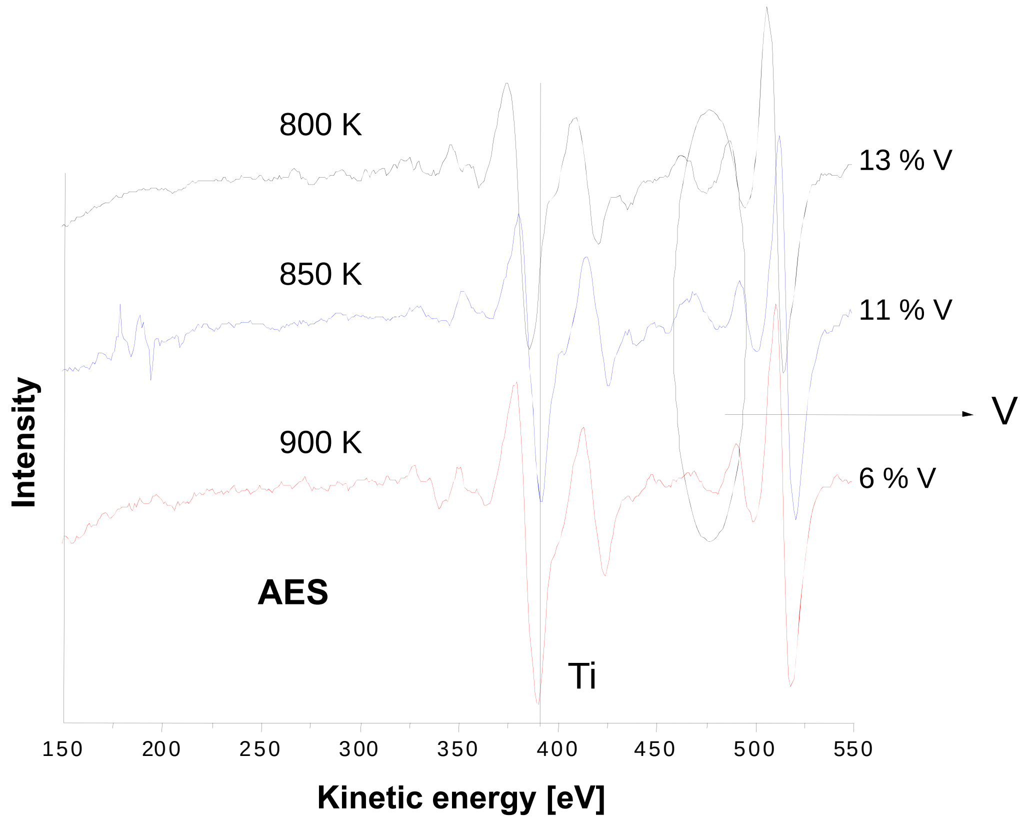
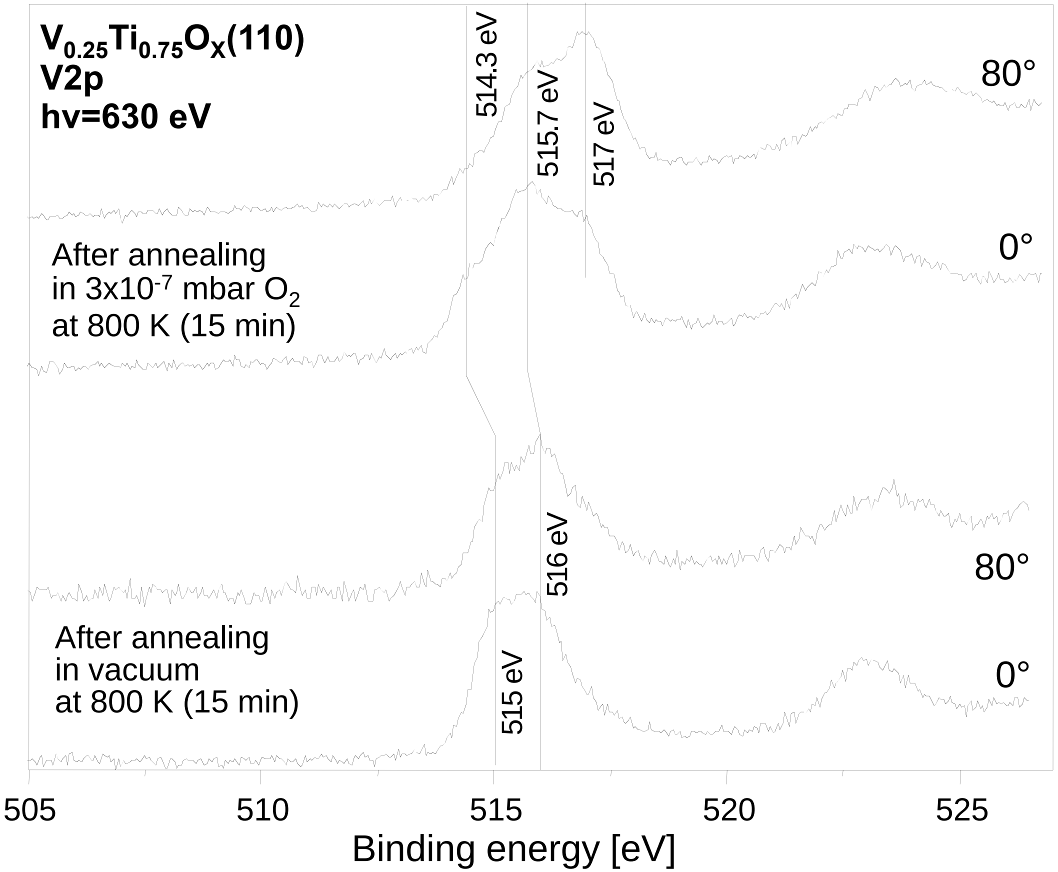
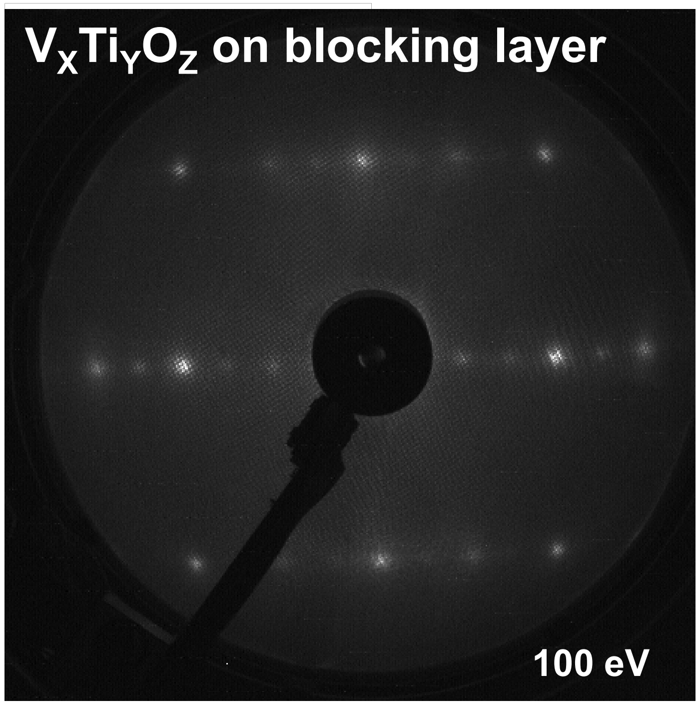


$V_XTi_YO_X$ on the blocking layer



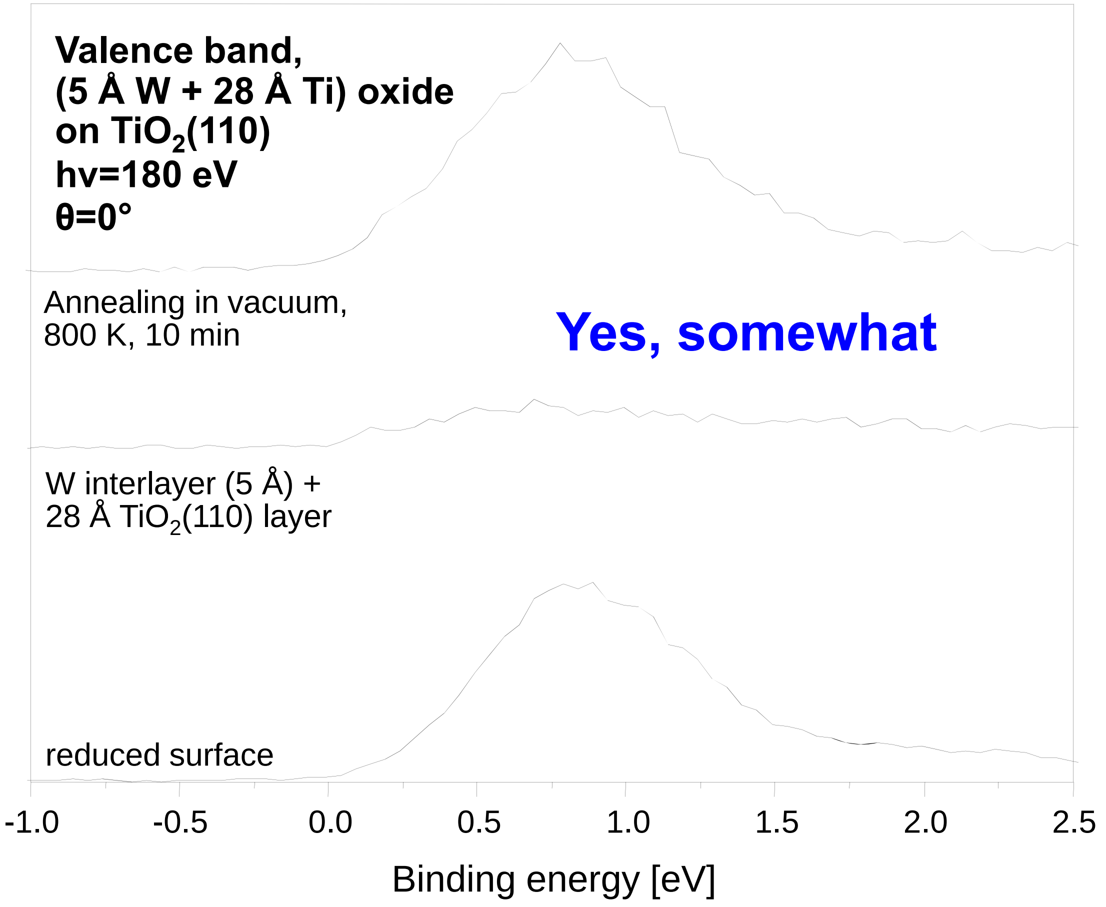


1x2 LEED pattern

Oxygen produces V^{5+} at the surface.

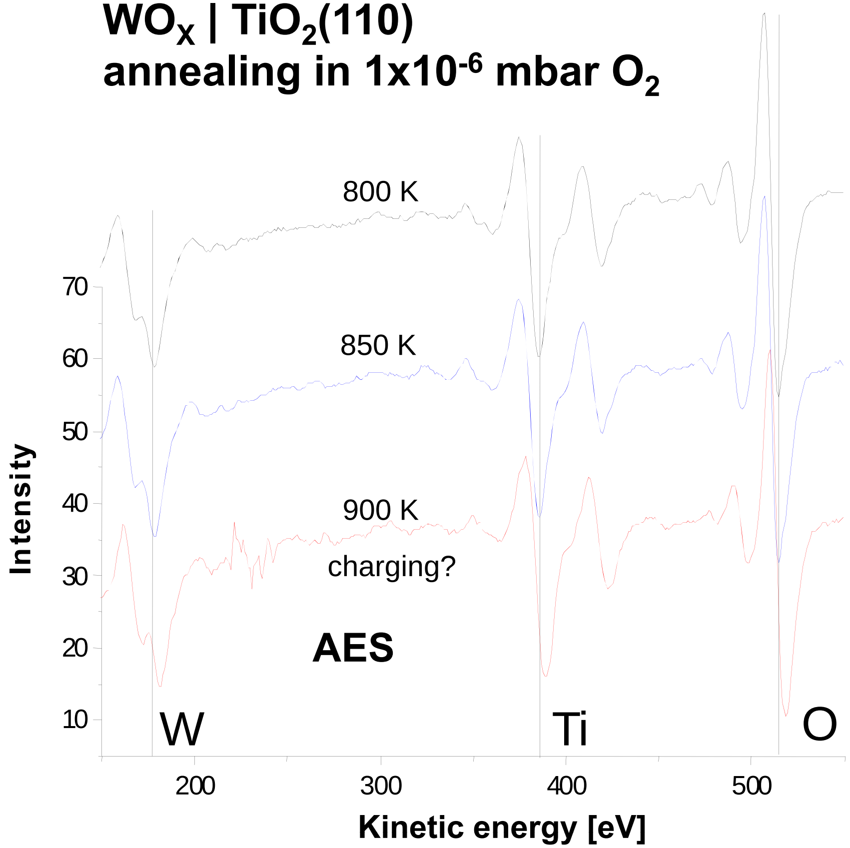
V^{3+} and V^{4+} below.

Does the blocking layer block defect diffusion?

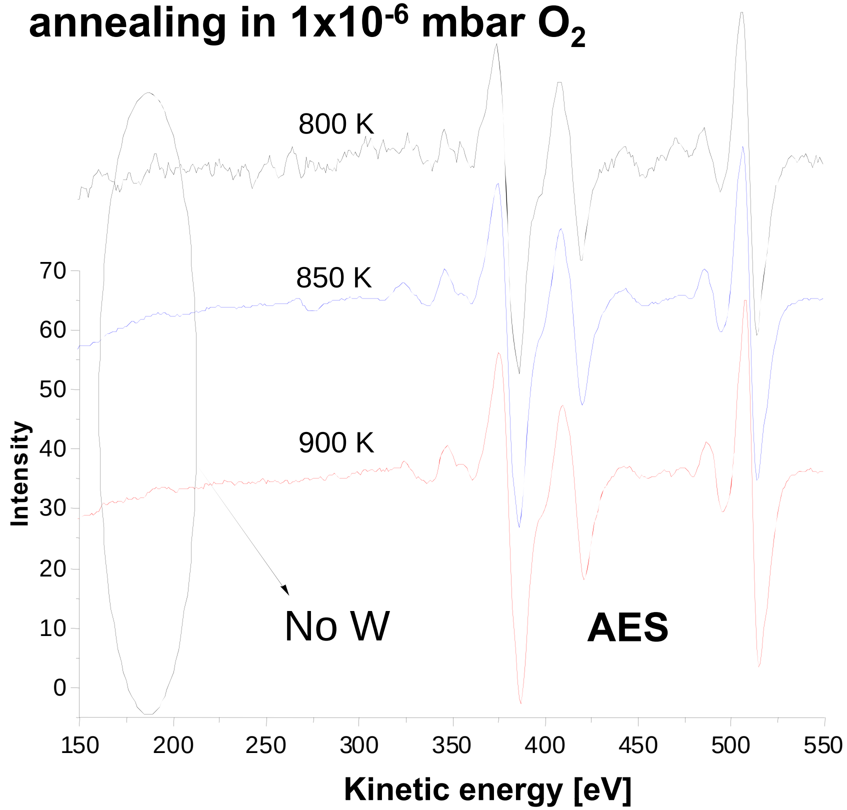


Thermal stability of the W+Ti oxide layer

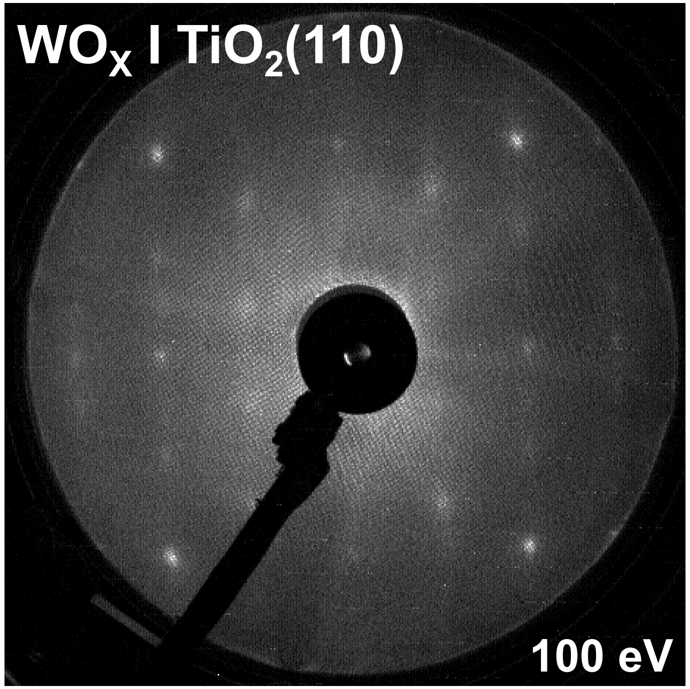
WO_X | TiO_2(110)
annealing in $1x10^{-6}$ mbar O_2



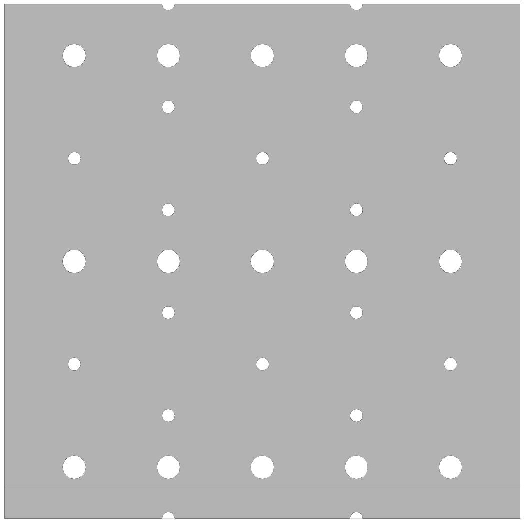
TiO_2(110) | WO_X | TiO_2(110)
annealing in $1x10^{-6}$ mbar O_2



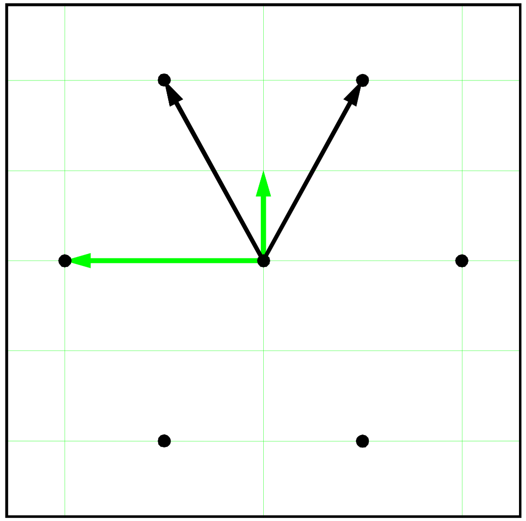
Tungsten oxide on TiO_2(110)



reciprocal space



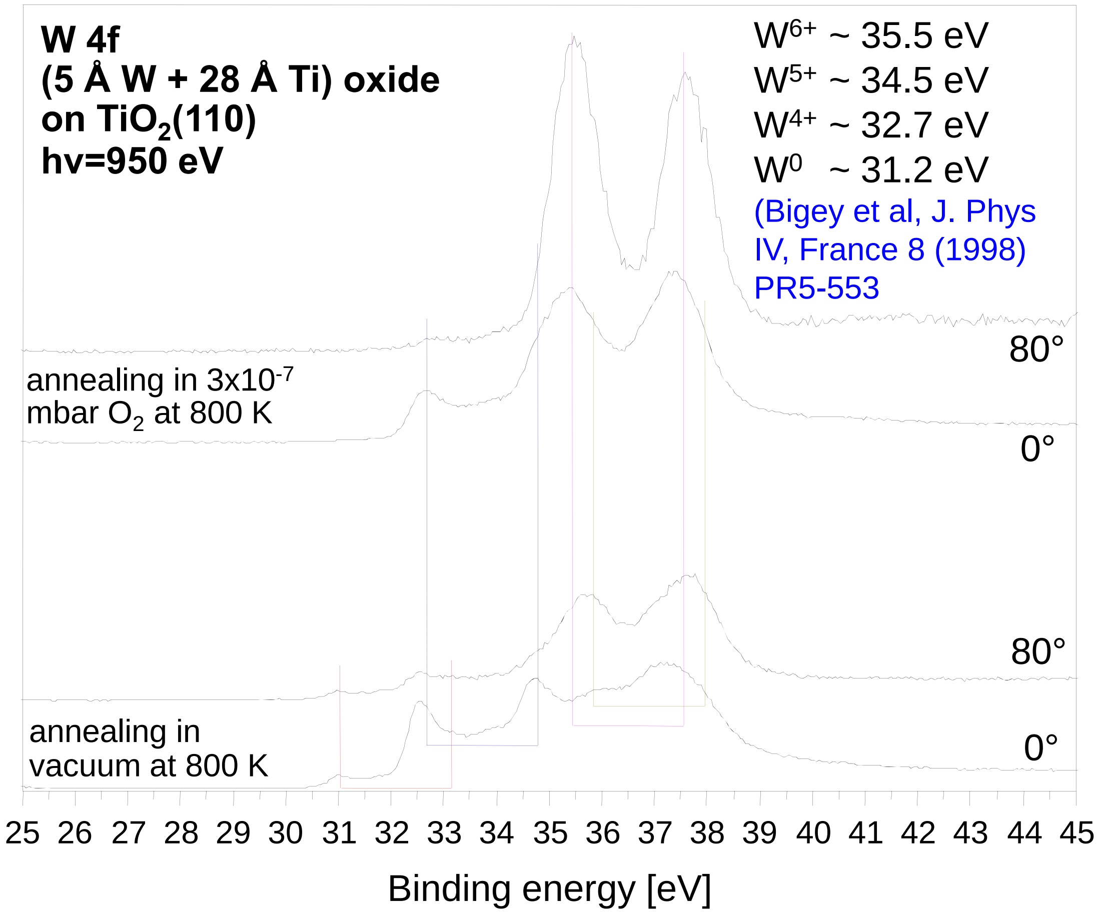
real space



C(4x1) structure, 6.8 Å lattice constant

LEED simulation with
LEEDpat 2.1, K. Hermann and M. A. van Hove

Thermal stability of the W+Ti oxide layer -2-



Annealing at 800 K in oxygen leads to the pile up of W^{6+} at the surface [est.: some percent]

Mainly W^{4+} in the bulk.

➔ Try another material as blocking layer

Summary

- Preparation of TiO_2(110) layers on Au and Pt substrates was not successful.
- TiO_2(110) and mixed oxide layers [V, Mo in TiO_2(110)] can be prepared and stabilized on TiO_2(110).
- Tungsten oxide diffusion blocking layer can hinder V and defect diffusion.
  - ➢ Blocking layer not fully stable.
- Tendency for Mo, V, and W mixed with TiO_2(110): oxygen treatment pulls out higher oxidation states [phase separation].
- More stable when annealed in vacuum.

Current effort

- Check whether lead [larger ionic diameter] can be used for the blocking layer.

Future

- Methanol adsorption.