

Distribution of O atoms on partially oxidized metal surfaces according to ab-initio calculations, and the consequences for sputtering of individual metal oxides

Jiri Houska and Tomas Kozak

*Department of Physics and NTIS - European Centre of Excellence,
University of West Bohemia, Czech Republic*



Acknowledgment

Grant Agency of the Czech Republic through Project No. 17-08944S

Motivation

- **Oxidation of metal targets** during sputtering of metal oxides



lower deposition rate due to

- (i) lower sputtering current density (except rf sputtering) and
- (ii) **lower sputtering yield of metal atoms** (for most metals)

TABLE IV
Comparison of sputtering behavior of oxides and metals for 10-keV Kr impact

Oxide	S for oxide (atoms/ion)	Ref.	S for metal (atoms/ion)	Ref.	$\frac{S_{\text{oxide}}}{S_{\text{metal}}}$	$\frac{S_{\text{oxide}}}{S_{\text{metal}}} \cdot x_{\text{metal}}$
Al ₂ O ₃	1.6; 1.4 ± 0.2 ^a	12; 6, 7, 8	3.2 ± 0.6 ^a	34-37	0.5	0.2
MgO	1.8 ± 0.5 ^a	3, 8	8.1 ^a	3	0.2	0.1
MoO ₃	9.6 ± 0.4	14	2.8 ± 1.0 ^a	34, 38, 39, 40	3.4	0.9
Nb ₂ O ₅	3.4 ± 0.5	13	1.6 ^a ; 2.0 ^b	39; 41	1.9	0.5
SiO ₂	4.2; 3.0 ± 1.5 ^a	14; 2, 6, 9	2.1 ^a	42	1.7	0.6
SnO ₂	15.3 ± 1.8	14, 15	6.7; 6.4 ± 0.6 ^a	22	2.3	0.8
Ta ₂ O ₅	2.5 ± 0.5	13	1.6 ± 0.3 ^a	34, 39, 43	1.6	0.4
TiO ₂	1.9; 1.4 ^a	12; 8	2.1 ± 0.8 ^a	36, 39, 44	0.8	0.3
UO ₂	3.8 ± 0.5 ^a	10	2.4 ^a	45	1.6	0.5
V ₂ O ₅	12.7 ± 1.7	14	2.3 ± 0.4 ^c	46	5.5	1.6
WO ₃	9.2 ± 1.2	13	2.6 ± 1.0 ^a	34, 38, 39, 40	3.6	0.9
ZrO ₂	2.8 ± 0.1	14	2.3 ^a	40	1.2	0.4

[R. Kelly et al., Radiation Effects 19 (1973) 39-47]

- **Catalysis**
- **Corrosion**

Motivation

- **Oxidation of metal targets** during sputtering of metal oxides



lower deposition rate

- Efforts to use optimum amount of reactive gas
(enough to deposit stoichiometric metal oxides, but no more)
and to work with **partially oxidized targets**

e.g. hundreds nm/min by pulsed O₂ flow control

[J. Vlcek, J. Rezek, J. Houska et al., Surf. Coat. Technol. 236 (2013) 550]

- Understanding and simulations of sputtering is based on quantities such as sputtering yield, oxygen binding energy, secondary electron emission coefficient
 - known for metal and stoichiometric oxide
 - **unknown for substoichiometric oxide**

Motivation

Literature:

- Some metals exhibit **monotonic** voltage when cleaning oxidized target
↓
weighted average of (e.g.) secondary el. emission coefficient for oxide and metal seems to be **good enough**
- Some metals exhibit **non-monotonic** voltage when cleaning oxidized target
↓
weighted average of (e.g.) secondary el. emission coefficient for oxide and metal is **not good enough**

Motivation

Literature:

- Some metals exhibit **monotonic** voltage when cleaning oxidized target

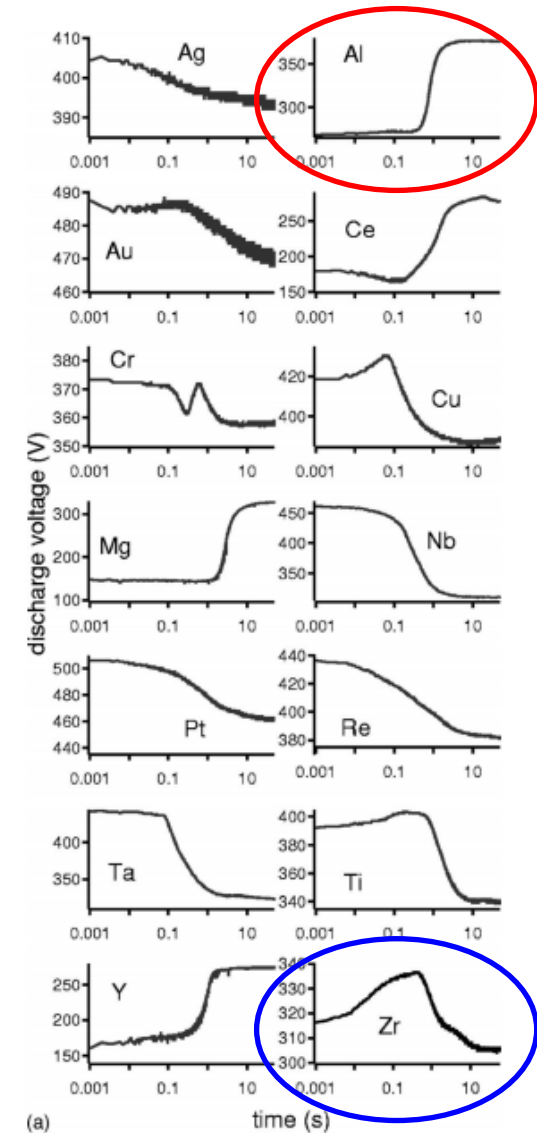


weighted average of (e.g.) secondary el. emission coefficient for oxide and metal seems to be **good enough (e.g. Al)**

- Some metals exhibit **non-monotonic** voltage when cleaning oxidized target



weighted average of (e.g.) secondary el. emission coefficient for oxide and metal is **not good enough (e.g. Zr)**



[D. Depla et al., J. Appl. Phys. 101 (2007) 013301]

Main aim

- Hypothesis: partially oxidized metal surfaces
 - for some metals constitute of a mixture of **stoichiometric oxide + metal** (\Rightarrow weighted average is OK)
 - for some metals constitute a homogeneous **substoichiometric oxide** (\Rightarrow weighted average is **not** OK)
- Let's predict which of these 2 cases happens for which metal **by ab-initio calculations**
- **Metals considered: Ti, Zr, Hf, Cu, Ag, Al**
 - technologically important
 - early TM Ti+Zr+Hf & noble metals Cu+Ag & main group Al
 - hcp Ti+Zr+Hf & fcc Cu+Ag+Al

Methodology of ab-initio calculations

- 48 metal atoms in **3 close packed layers per 16 atoms**
 - i.e. hcp (0001) or fcc (111)
 - periodical boundaries in horizontal directions
 - vacuum slab above the surface
- Oxygen adsorption energy (E_{ads}) for partially oxidized surface ($0 < \text{oxygen atoms} < 16$) after geometry optimization
- PWscf code (Quantum Espresso package)
 - Vanderbilt ultrasoft pseudopotentials
 - PBE xc functional
 - wavefunction & density cutoff of 25 & 300 Ry
 - $3 \times 3 \times 1$ k-points
- E_{ads} error up to ~2% only, no effect on E_{ads} trends

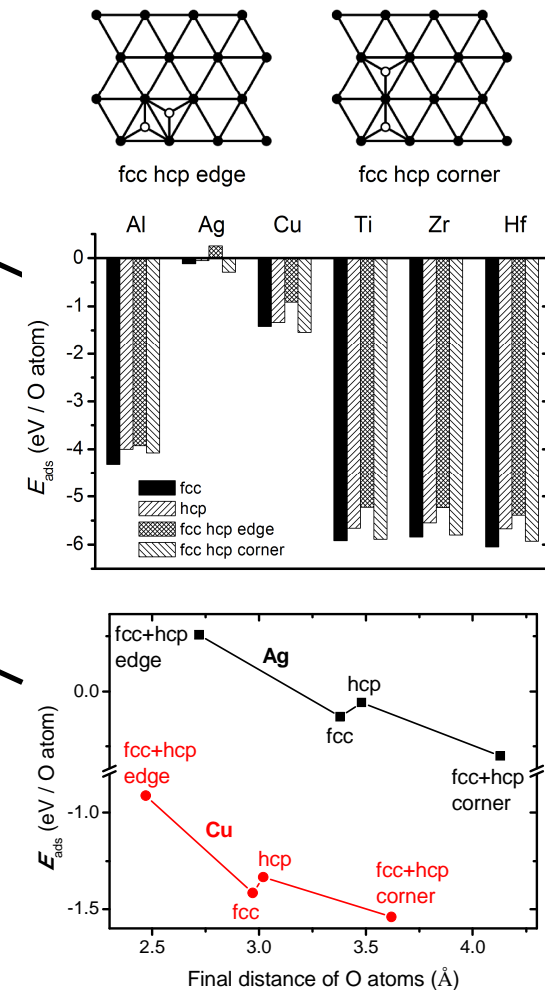
Adsorption sites of O atoms

- One adsorbed O molecule \Rightarrow two close O atoms at :
2×fcc, 2×hcp, fcc+hcp sharing edge, fcc+hcp sharing corner

- Non-noble metals (Ti, Zr, Hf, Al):
lowest E_{ads} for two fcc sites
- Noble metals (Cu, Ag):
low preference to oxidize \Leftrightarrow **lower E_{ads} for more distant O atoms**
(rather than dependence on fcc/hcp)

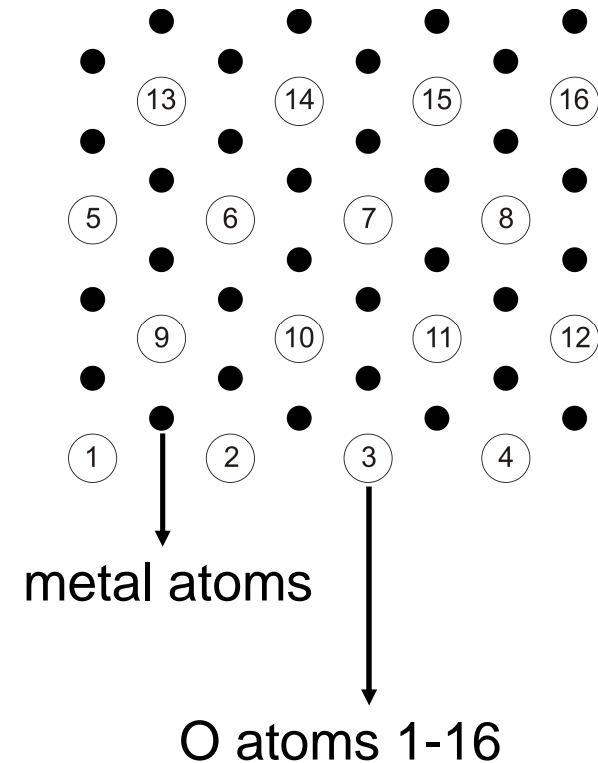
- Hcp sites never preferred,
even for hcp metals

\Downarrow
Fcc sites considered below



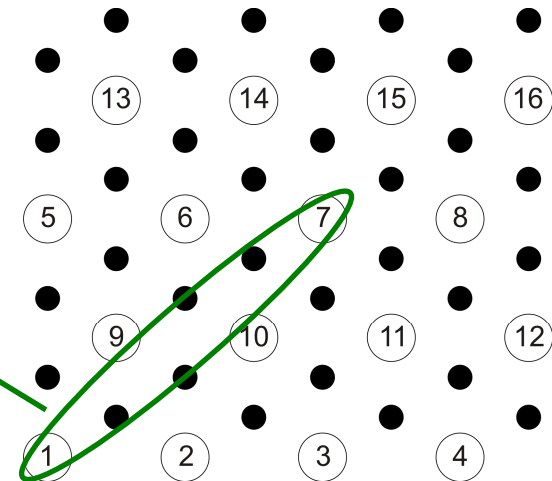
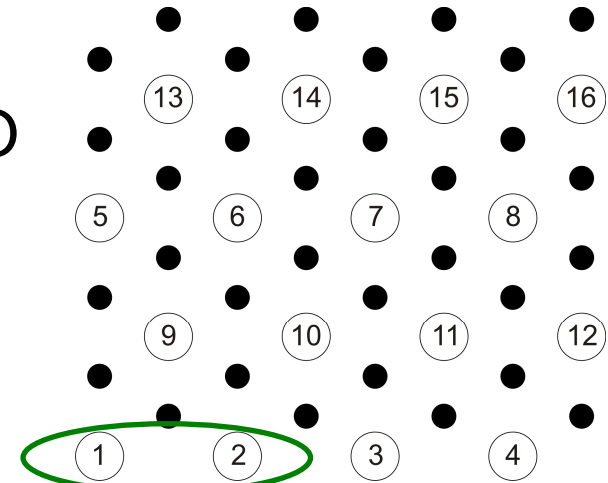
Results: E differences for different O configurations

- O atom configurations characterized by **total squared quadratic distance (D)** of O atoms
- O adsorption energy calculated for all surface coverages $\Theta_{\text{O}} = 2/16$ to $14/16$ and **all configurations of O atoms (all D values)**



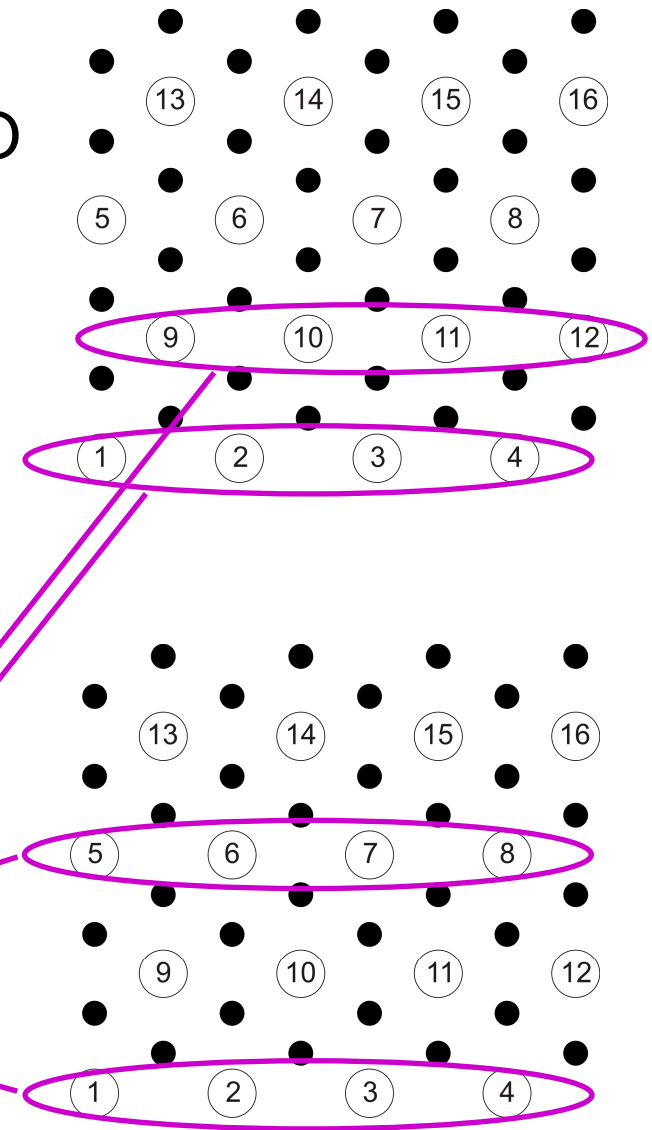
Results: E differences for different O configurations

- O atom configurations characterized by total squared quadratic distance (D) of O
- O adsorption energy calculated for all surface coverages $\Theta_O = 2/16$ to $14/16$ and all configurations of O atoms
- $\Theta_O = 2/16$: 4 configurations between $D = 0.5 a^2$ (atoms 1,2) and $D = 3.5 a^2$ (atoms 1,7) where a = fcc lattice const.



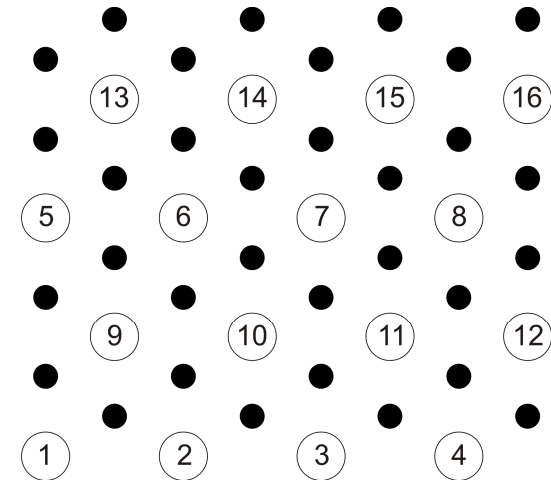
Results: E differences for different O configurations

- O atom configurations characterized by total squared quadratic distance (D) of O
 - O adsorption energy calculated for all surface coverages $\Theta_O = 2/16$ to $14/16$ and all configurations of O atoms
 - $\Theta_O = 2/16$: 4 configurations between $D = 0.5 a^2$ (atoms 1,2) and $D = 3.5 a^2$ (atoms 1,7)
 - $\Theta_O = 8/16$: 31 configurations between $D = 28 a^2$ (atoms 1-4 & 9-12) and $D = 48 a^2$ (atoms 1-4 & 5-8)
- where a = fcc lattice const.



Results: *E* differences for different O configurations

- O atom configurations characterized by total squared quadratic distance (D) of O
- O adsorption energy calculated for all surface coverages $\Theta_O = 2/16$ to $14/16$ and all configurations of O atoms
- $\Theta_O = 2/16$: 4 configurations between $D = 0.5 a^2$ (atoms 1,2) and $D = 3.5 a^2$ (atoms 1,7)
- $\Theta_O = 8/16$: 31 configurations between $D = 28 a^2$ (atoms 1-4 & 9-12) and $D = 48 a^2$ (atoms 1-4 & 5-8)
- All coverages $\Theta_O = 2/16$ to $14/16$:
235 configurations (and ab-initio calculations) **per metal**



Results: E differences for different O configurations

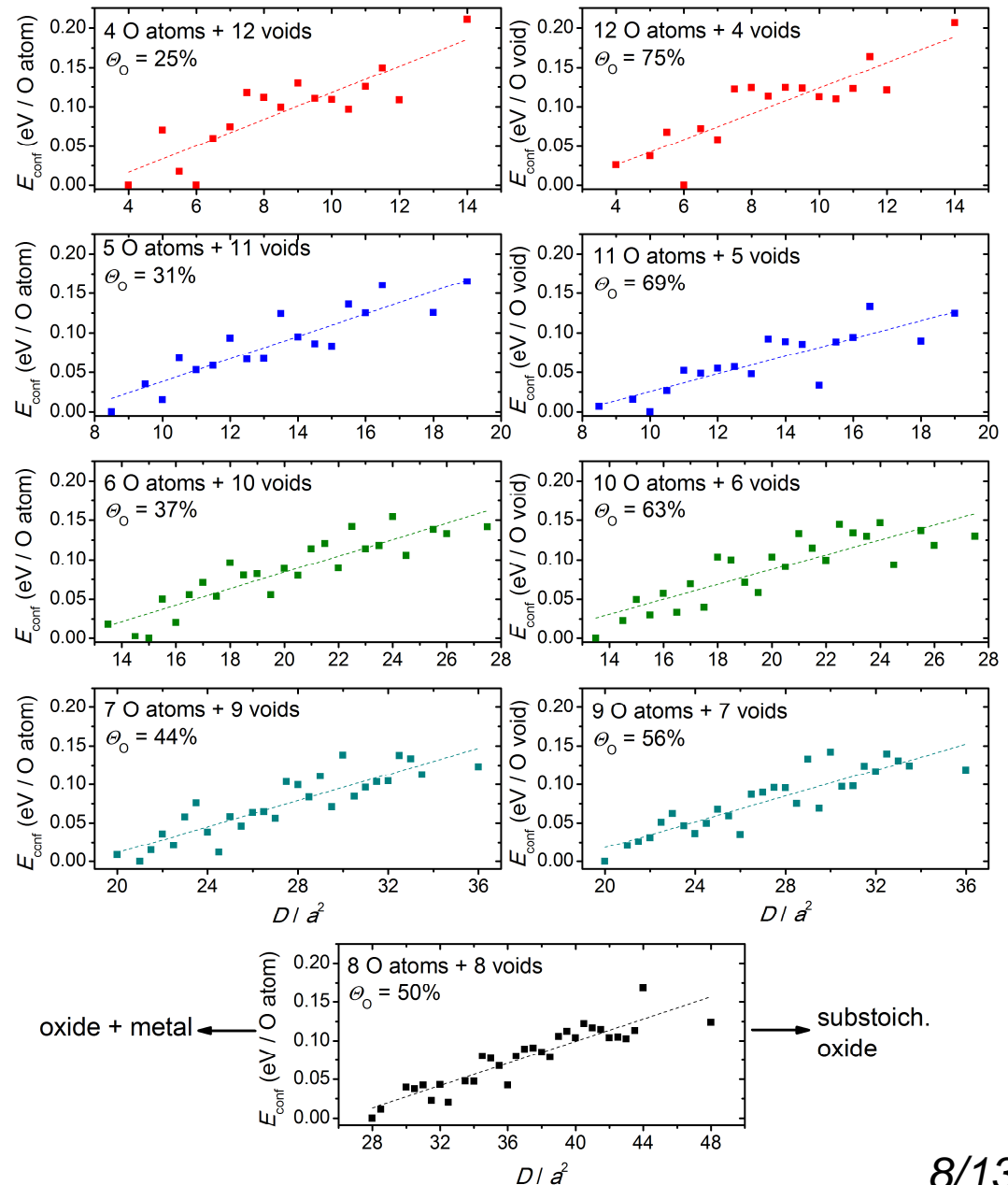
- Shown with respect to preferred configuration ($E_{\text{conf}} = E_{\text{ads}} - E_{\text{ads_min}}$)

- Example for Al** and $\Theta_{\text{O}} = 4/16$ to $12/16$

- Lowest E_{conf} for low D



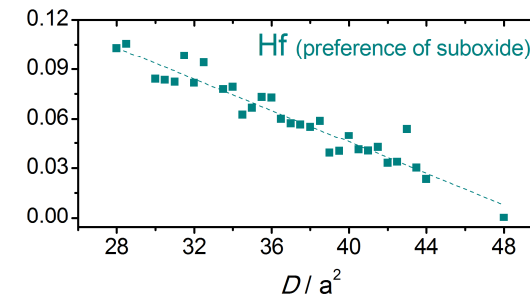
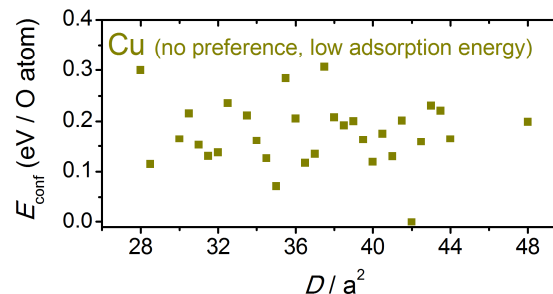
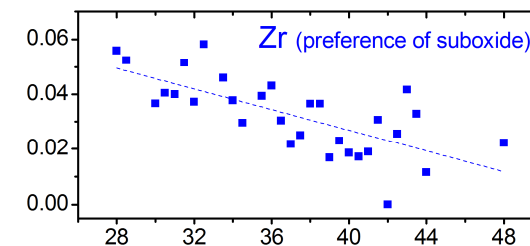
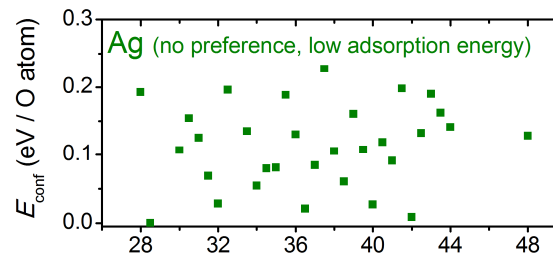
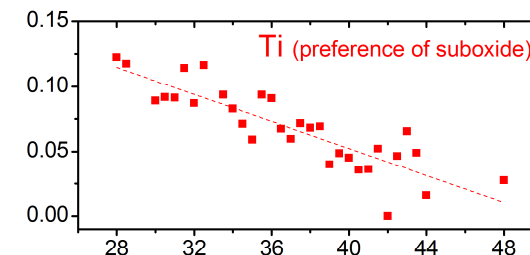
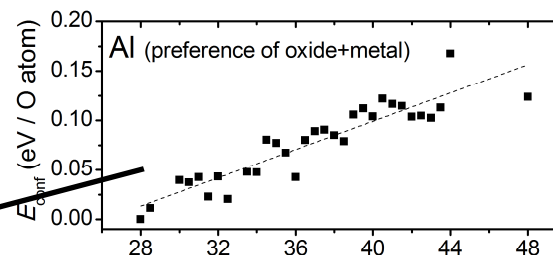
preference towards
a mixture of stoich.
oxide + metal
(independently of Θ_{O})



Results: E differences for different O configurations

- $E_{\text{conf}} = E_{\text{ads}} - E_{\text{ads_min}}$
shown for 6 metals
at $\Theta_{\text{O}} = 8/16$

- **Al:** \leftarrow
low $D \Rightarrow$ mixture
of oxide + metal

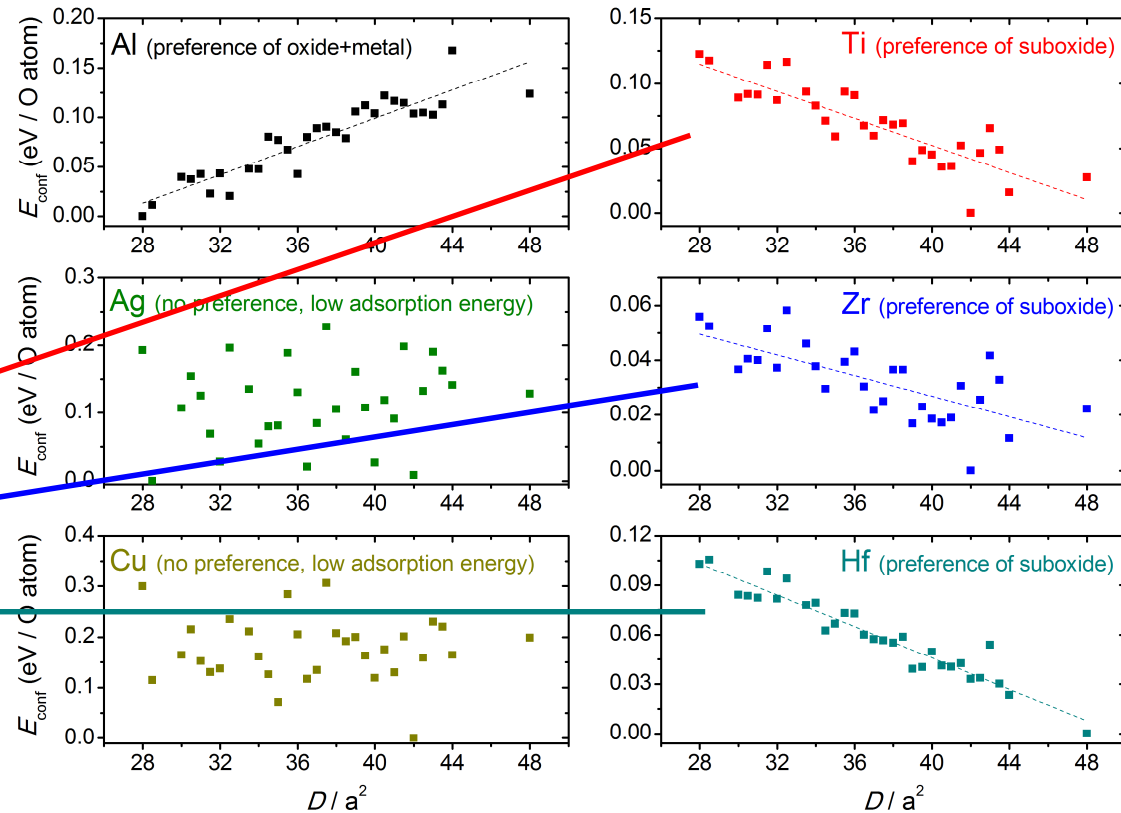


Results: E differences for different O configurations

- $E_{\text{conf}} = E_{\text{ads}} - E_{\text{ads_min}}$
shown for 6 metals
at $\Theta_{\text{O}} = 8/16$

- **Al:**
low $D \Rightarrow$ mixture
of oxide + metal

- **Ti, Zr, Hf:**
high $D \Rightarrow$
homogeneous
suboxide



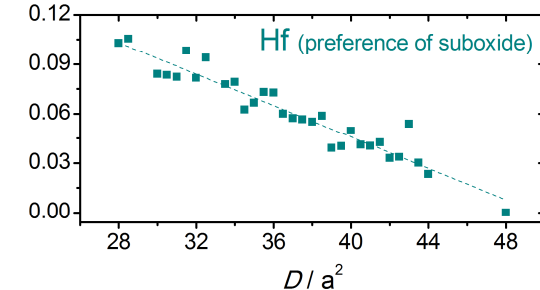
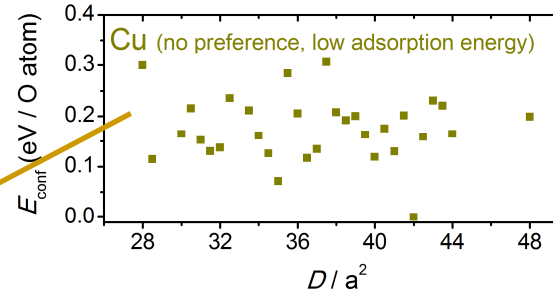
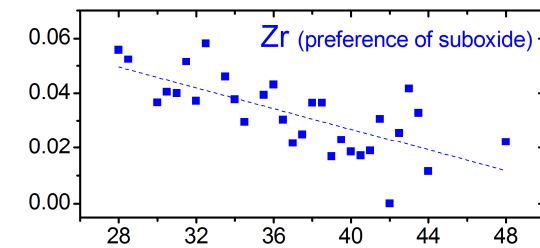
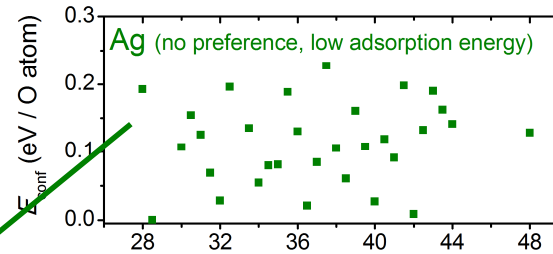
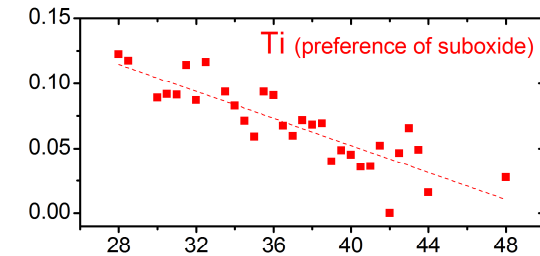
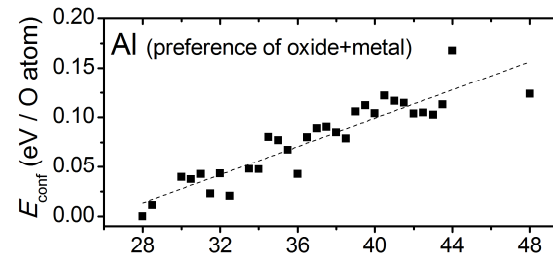
Results: E differences for different O configurations

- $E_{\text{conf}} = E_{\text{ads}} - E_{\text{ads_min}}$
shown for 6 metals
at $\Theta_{\text{O}} = 8/16$

- **Al:**
low $D \Rightarrow$ mixture
of oxide + metal

- **Ti, Zr, Hf:**
high $D \Rightarrow$
homogeneous
suboxide

- **Ag, Cu:**
low adsorption energy,
no strong preference



Results: agreement with formation enthalpies of MO_x

Stoichiometry	H (kJ / mole of struct. units)	H (kJ / mole of O atoms)	H (kJ / mole of M atoms)
Al_2O_3	1676	559	838
Al_3O_4	1995	499	665
AlO	363	363	363
TiO_2	944	472	944
Ti_2O_3	1598	533	799
ZrO_2	1106	553	1106
Zr_2O_3	1666	555	833
HfO_2	1166	583	1166
Hf_2O_3	1700	567	850

- **enough oxygen:** H per metal atom increases with $x \Rightarrow$ preference of stoichiometric Al_2O_3 , TiO_2 , ZrO_2 , HfO_2

Results: agreement with formation enthalpies of MO_x

Stoichiometry	H (kJ / mole of struct. units)	H (kJ / mole of O atoms)	H (kJ / mole of M atoms)
Al_2O_3	1676	559	838
Al_3O_4	1995	499	665
AlO	363	363	363
TiO_2	944	472	944
Ti_2O_3	1598	533	799
ZrO_2	1106	553	1106
Zr_2O_3	1666	555	833
HfO_2	1166	583	1166
Hf_2O_3	1700	567	850

- **enough oxygen:** H per metal atom increases with $x \Rightarrow$ preference of stoichiometric Al_2O_3 , TiO_2 , ZrO_2 , HfO_2
- **lack of oxygen for Al:** H per O atom increases with $x \Rightarrow$ preference of Al_2O_3 + metal over a suboxide (e.g. Al_3O_4 , AlO)

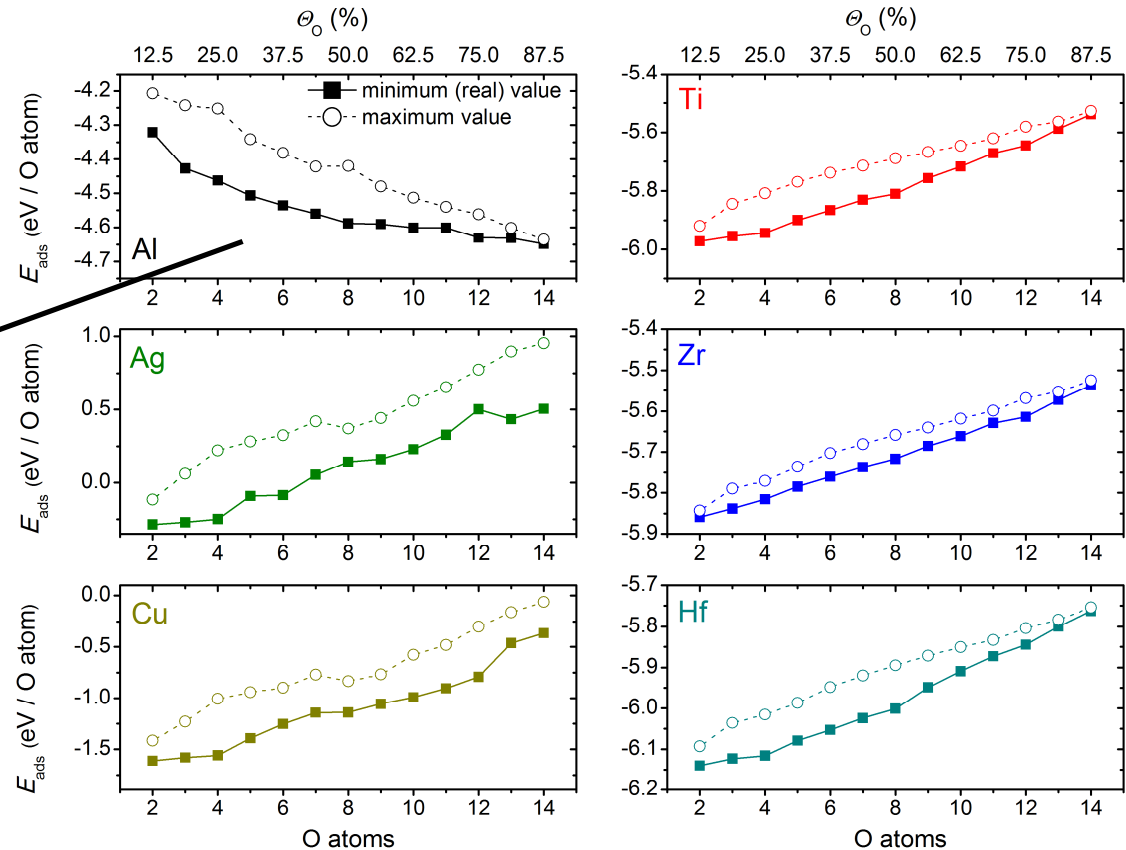
Results: agreement with formation enthalpies of MO_x

Stoichiometry	H (kJ / mole of struct. units)	H (kJ / mole of O atoms)	H (kJ / mole of M atoms)
Al_2O_3	1676	559	838
Al_3O_4	1995	499	665
AlO	363	363	363
TiO_2	944	472	944
Ti_2O_3	1598	533	799
ZrO_2	1106	553	1106
Zr_2O_3	1666	555	833
HfO_2	1166	583	1166
Hf_2O_3	1700	567	850

- **enough oxygen:** H per metal atom increases with $x \Rightarrow$ preference of stoichiometric Al_2O_3 , TiO_2 , ZrO_2 , HfO_2
- **lack of oxygen for Al:** H per O atom increases with $x \Rightarrow$ preference of Al_2O_3 + metal over a suboxide (e.g. Al_3O_4 , AlO)
- **lack of oxygen for Ti, Zr, Hf:** H per O atom less dependent on x (Zr, Hf) or even decreases with x (Ti) \Rightarrow preference of homogeneous suboxide (e.g. Ti_2O_3) over TiO_2 + metal

Results: Adsorption energy

- E_{ads} affected by O atom configuration (full \times empty symbols)
- E_{ads} affected by surface coverage Θ_{O}
- **Al:** $|E_{\text{ads}}|$ increases with increasing Θ_{O} (positive feedback)



atomic scale preference towards stoichiometric oxide + metal
 \Leftrightarrow macroscopic preference to complete the oxidation

more horizontal $E_{\text{ads}}(\Theta_{\text{O}})$ expected for larger oxide and metal zones (lower importance of the edges)

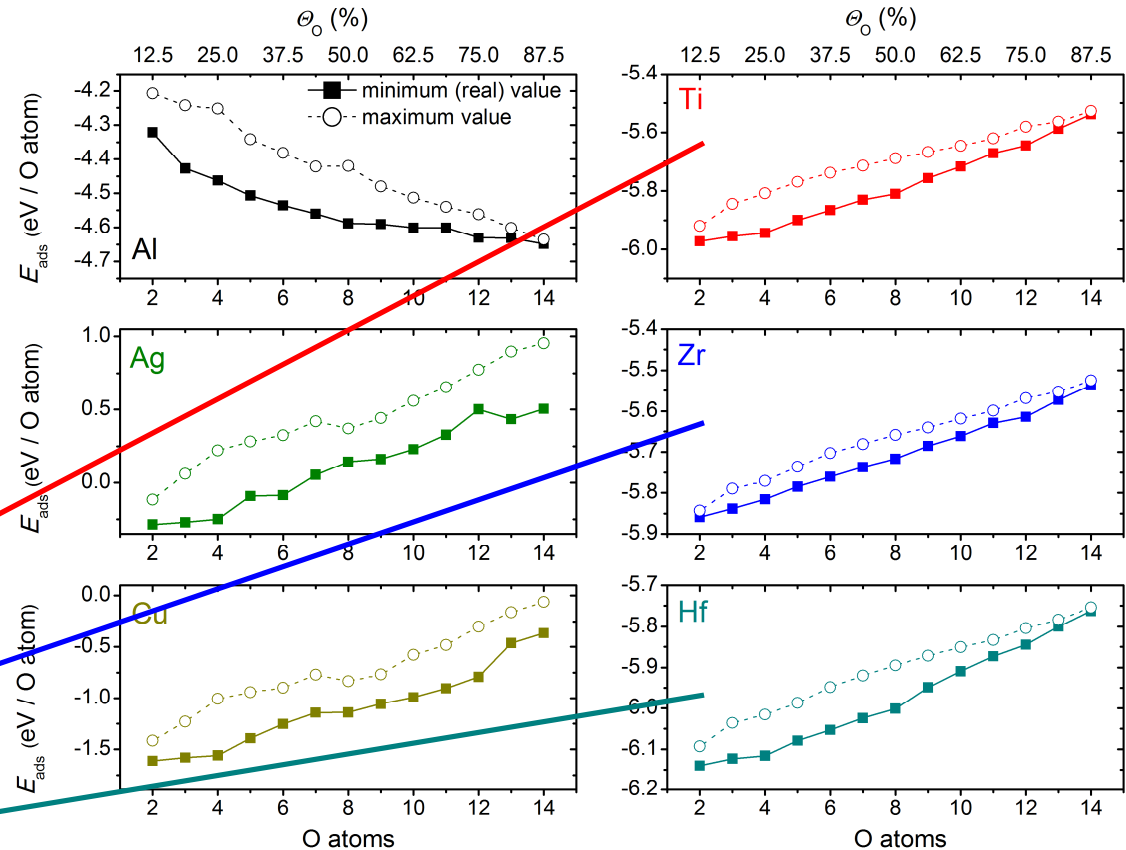
Results: Adsorption energy

- E_{ads} affected by O atom configuration (full \times empty symbols)

- E_{ads} affected by surface coverage Θ_{O}

- **Al:**
| E_{ads} | increases with increasing Θ_{O} (positive feedback)

- **Ti, Zr, Hf:**
| E_{ads} | decreases with increasing Θ_{O} (negative feedback; opposite behavior to Al on both scales)



Results: Adsorption energy

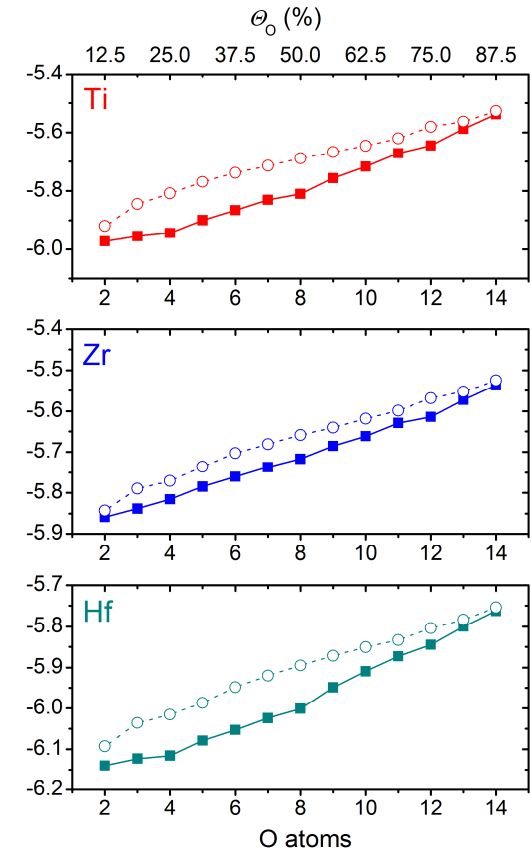
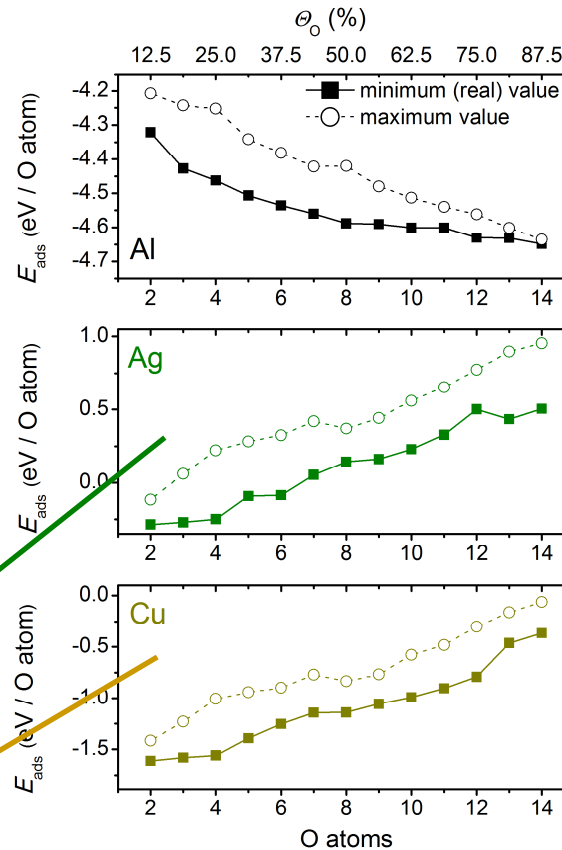
- E_{ads} affected by O atom configuration (full \times empty symbols)

- E_{ads} affected by surface coverage Θ_{O}

- **Al:**
 $|E_{\text{ads}}|$ increases with increasing Θ_{O}

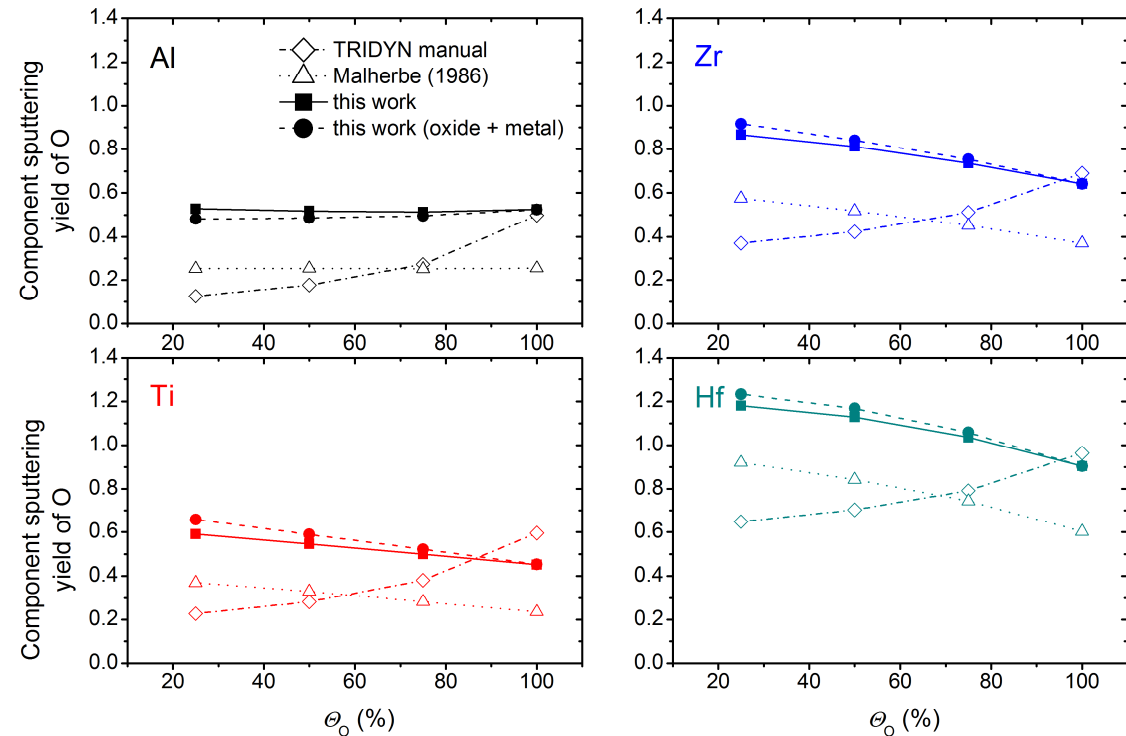
- **Ti, Zr, Hf:**
 $|E_{\text{ads}}|$ decreases with increasing Θ_{O}

- **Ag, Cu:**
 $|E_{\text{ads}}|$ decreases with increasing Θ_{O}
 E_{ads} close to zero (Cu) or even positive (Ag) at high Θ_{O}



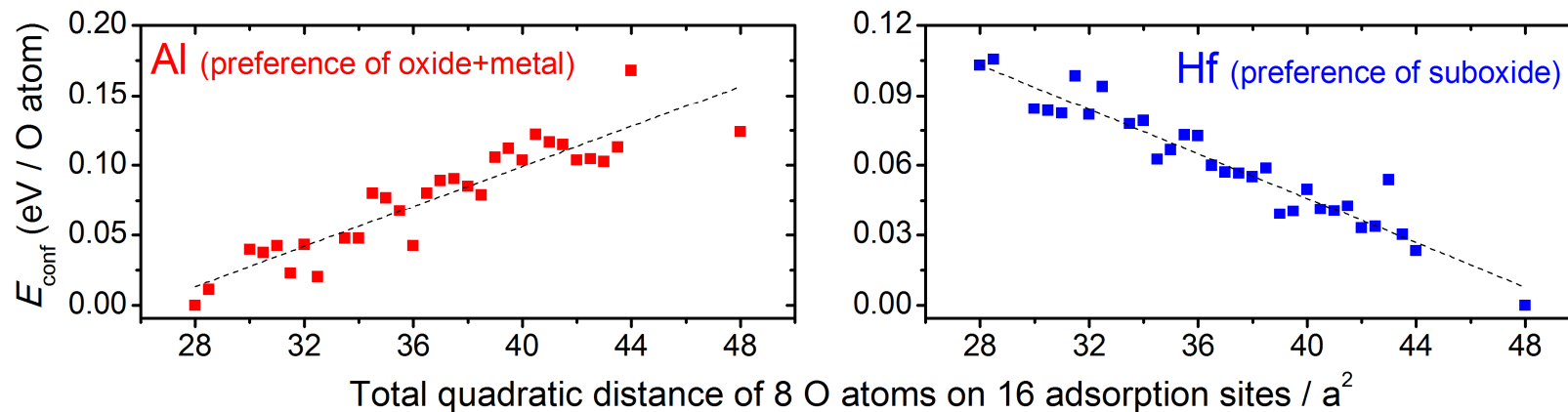
Results: Using adsorption energy for sputtering yields

- Binary collision approximation Monte Carlo method using SDTrimSP program
- Using (i) E_{ads} from previous slides and (ii) E_{ads} from other sources
- Importance of
 - E_{ads} values themselves
 - $E_{\text{ads}}(\theta_{\text{O}})$ dependence
 - O atom configuration (full squares \times full balls)



Conclusions

- Preferred O atom configurations on partially oxidized metals
- Al: preferred mixture of stoichiometric oxide + metal
- Ti, Zr, Hf: preferred homogeneous suboxide, weighted average of oxide and metal properties is not good enough
- Correlation with formation enthalpies of oxides & suboxides
- E_{ads} used for sputtering yield calculations



[J. Houska and T. Kozak, J. Appl. Phys. 121, 225303 (2017)]