Activities within the Be-CRP 2013/14

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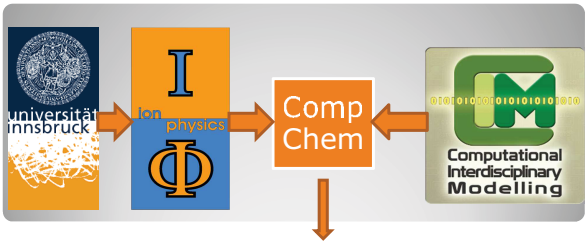


Ivan Sukuba (Comenius University Bratislava)
Michael Probst
Jan Urban
Alexander Kaiser
Stefan Huber
Michael Gyoerek

Topics:

1. **Molecular Dynamics Simulations of sputtering of Be_nW (n=2,12)** (Ivan Sukuba, continued work in progress)
2. Calculations of thermodynamic data of BeD_n formation reactions (I.Sukuba)
3. Electron impact cross section calculations of Be-species (in progress, not mentioned here; I. Sukuba & A. Kaiser)
4. Comparison of vacancy formation and C-adsorption energies between Al and Be (A. Kaiser, 1st part published 2014)
5. Energy barriers for the intrusion of BeH_x into graphite. (S.Huber, published 2014, not here)

MD of Be-D sputtering (Ivan Sukuba)

Alloys:

1) Be_2W surface
(hpc, 2940 atoms ~30x30x40 A)
1000 D impacts (NVE, pseudo-thermostat around the surface at 300 K, 7 ps
3 ps impact + 4 ps relaxation)

2) $Be_{12}W$ surface
(hpc, 3328 atoms ~30x30x40 A)
1000 D impacts (NVE, pseudo-thermostat around the surface at 300 K, 7 ps
3 ps impact + 4 ps relaxation)

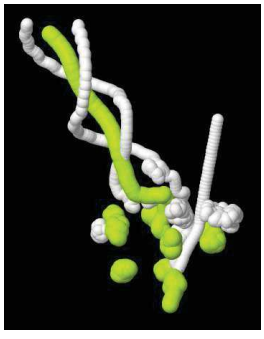
impact energies:
10, 12, 15, 20, 25, 30 eV

Some typical reactive events

- Only atoms with higher-than-normal kinetic energy are shown.
- For clarity, the rest of the (~3000) Be atoms is not shown.

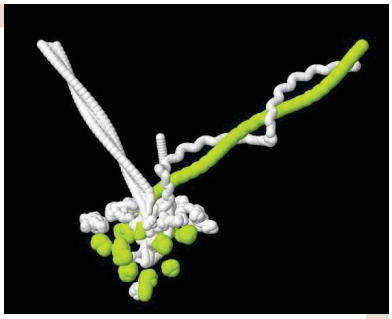
Typical trajectory 1:

- 10eV D-impact
- Formation of rotationally
- Excited BeH_2
- 'Benorm4H751'

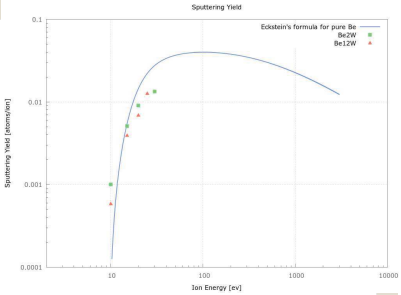


Typical trajectory 2:

- 10eV D-impact
- Formation of rotationally
- Excited BeH and D_2
- 'BeSEewnorm4H919'



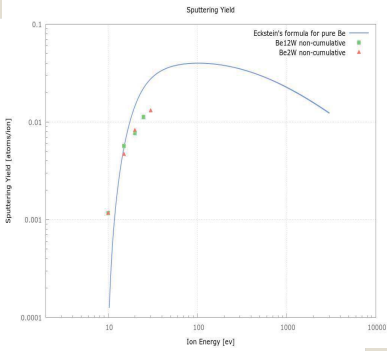
- Cumulative sputtering simulations
- Sputtering yield for alloys is similar to the one for pure Be. (which is similar to the Eckstein curve)
- Only Be-sputtering is observed. W is not sputtered.



- Be_2W sputtering slightly larger than $Be_{12}W$ sputtering.

(A preliminary version with less data was shown last year)

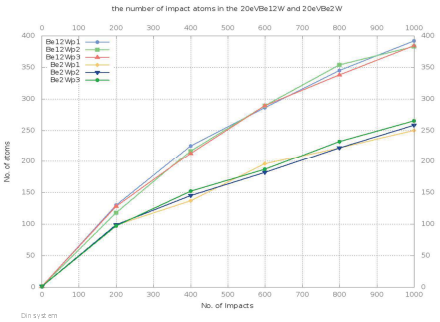
- New: Non-cumulative sputtering: Independent trajectories
- Sputtering yield for alloys is similar to the cumulative case.
- Only Be-sputtering is observed. W is not sputtered.



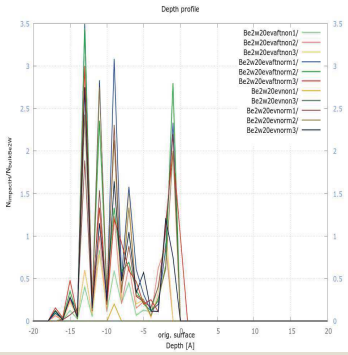
- Again, nearly no difference between Be_2W and $Be_{12}W$ sputtering.

Amount of D kept in(on) Be-W surfaces at 20 eV.

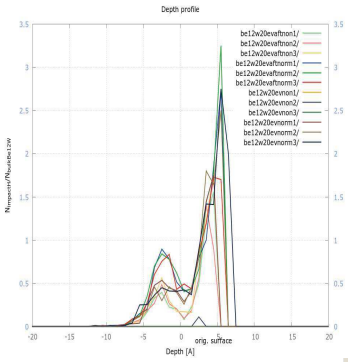
- In $Be_{12}W$ are the rates higher than Be_2W: Be_2W: ~25% ; $Be_{12}W$ ~45%



- D impacting with 20eV to Be_2W
- Depth profile at the end of 1000 impacts
- 'finaldepthprofileBe2w20ev'



- D impacting with 20eV to $Be_{12}W$
- Depth profile at the end of 1000 impacts
- 'finaldepthprofileBe12w20ev'



Topics:

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2) Calculation of free energies of Be-D formation reactions

ΔH as f(T) [kJ/Mol]

(B3LYP/ aug-cc-p(C)VTZ and MP2/ aug-cc-p(C)VTZ calculations)

Summary

- BeD_3 is not very stable in plasma conditions.
- D_2 formation gains much energy, preferring such reactions.
- Same with free energy ΔG.

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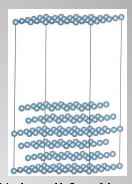
How similar are Al and Be ? Comparison of some aspects of their surface energetics

alkaline earth metal: Be(0001) hcp	p-group metal: Al(111) fcc

- The metals are structurally similar. Be is the lowest-Z metal.
- Comparison of Al and Be of interest because Al might serve as proxy for toxic Be in some experiments.
- **We calculate the stability against sputtering in terms of the energy needed to remove/replace one, three or seven surface atoms.**

Computational Details

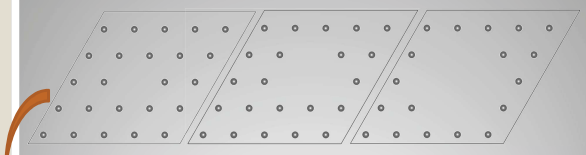
- PL-DFT in *Vasp 5.2*, energy cutoff 415 eV
- PAW pseudopotentials with PBE density functional and Grimme dispersion correction
- Gamma point sampling for large cells
- Vacuum thickness: 14 Å
- 5x5x(2+4) for Al, 8x8x(2+4) for Be
- Local optimization, 4 top layers fully relaxed
- Check of method with lattice constants, cohesive energies (CE), work functions (WF) and surface energies (SE)



Unit cell for Al

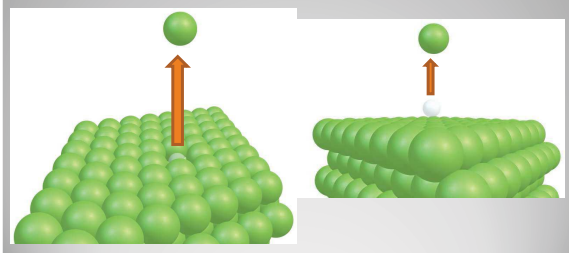
	a/c	lit.	CE	lit.	WF	lit.	SE	lit.
Al	4.013	4.04	3.7 3	3.23-4.21	4.1 3	4.24-4.54	1.1	0.94-1.27
Be								

Illustration of Vacancy Adatom Formation



2 7(0)

Binding energy of surface atoms



(0) (V)

Energy needed for taking an atom and putting it elsewhere on the surface. (=vacancy adatom formation)

	v	E_{va}/ eV
Al		
Be		4.88

- Energies larger for Be.
- Melting points: Be (1551 K)> Al (933 K)
- fewer bonds-to-neighbors have to be broken for larger v.
- costs for removing additional atoms becomes cheaper with v.
- Good agreement with literature data for vacancy formation energies of Al.

Adatom and vacancy binding energies

	v	E_{bad}/ eV	E_{bvac}/ eV
Al			
Be		3.01	5.11
	3	10.16	13.92
	7	24.84	29.72

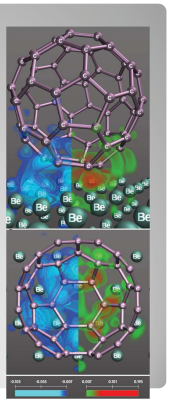
- E_{bvac}: Energy needed to put regular surface atoms into vacuum.
- E_{bad}: Energy needed to put additional surface atoms (adatoms) into vacuum.
- E_{bvac} larger for Be (5.11 eV)
- Increases with v since atoms are "individually" removed to vacuum.
- E_{bad} also larger for Be (3.1 eV)

Adsorption of C_{60}

	Al(111)				Be(001)			
V					0	1	3	7
D	1.99	3.97	4.28	3.44	2.45	3.69	4.21	3.58
q_{CT}	-2.3	-4.2	-4.1	-5.2	-4.8	-4.3	-5.2	-6.1
n_{ca}	6	6	4	6	6	6	9	9

D ... Dissociation energies (eV) q_{CT} ... Bader charge transfer (e)

- Van der Waals forces cannot be neglected [1]
- Be interacts more strongly here as well.

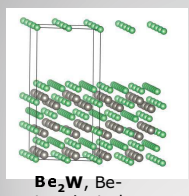


Current state:

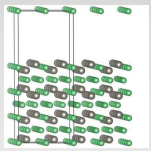
- **Main conclusion: Energetics similar but Be-Be and Be-C surface interactions stronger than Al-Al and Al-C.**
- Work published: DOI 10.1039/c4nr02717e (Nanoscale 2014)
- Additional questions to be solved:
  - Which energy is needed to remove, for example, a three-atoms cluster at once from the surface ?
  - How large ist the deformation of the surface due to vacancies ?
- Similar Calculations with the Be-W alloys are in progress (next page).

- Same methods and questions as for Be and Al

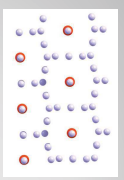
Surface energies of Be/W alloys



Be_2W, Be-terminated



Be_2W, W-terminated



$Be_{12}W$, Be-terminated

Contributors:

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- Pavel Mach (CU)
- Ivan Sukuba (CU)
- Andreas Mauracher (UI)
- Stefan Huber (UI)
- Thana Maihom (KU)
- Alexander Kaiser (UI)

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Vacancy patterning and patterning vacancies: controlled self-assembly of fullerenes on metal surfaces
Alexander Kaiser, Francesc Viñes, Francesc Illas, Marcel Ritter, Frank Hagelberg and Michael Probst
Nanoscale 2014 DOI: 10.1039/C4NR02717E

Thank you ...