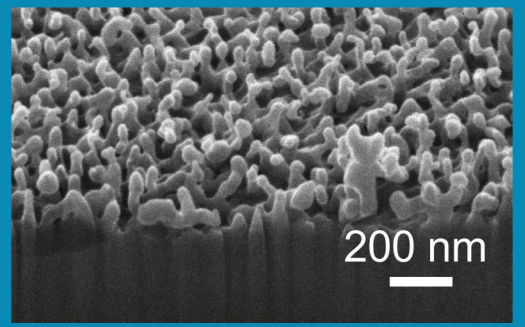
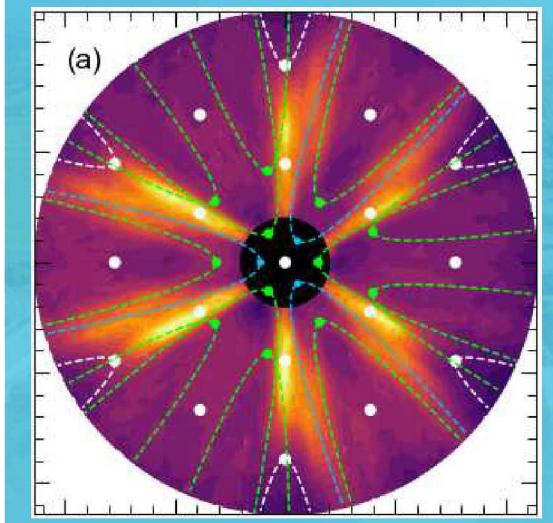
SAND2019-14315PE

Hydrogen and helium interactions with tungsten surfaces





PRESENTED BY

Tim Wong, Robert Kolasinski, and Josh Whaley

Sandia National Laboratories, California

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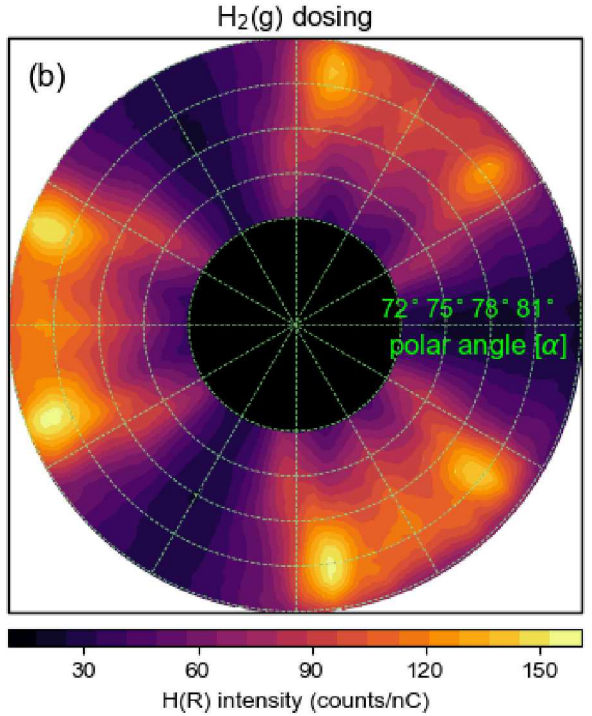
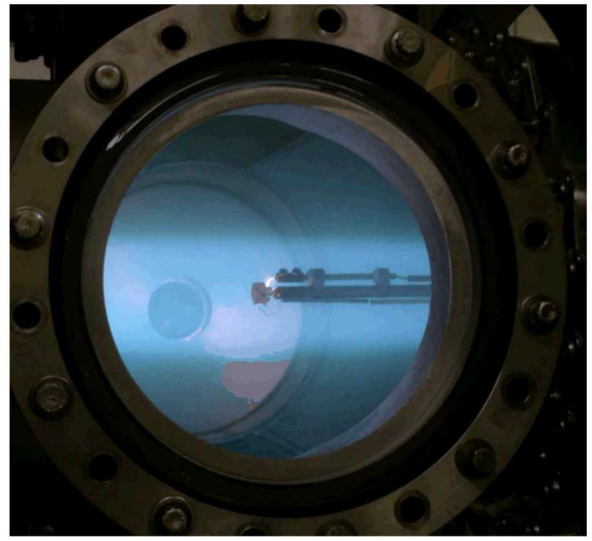
Outline: Hydrogen effects on materials

- Fusion energy
- H adsorption on W(111)
- High-temperature annealing of He-induced W fuzz
- Summary





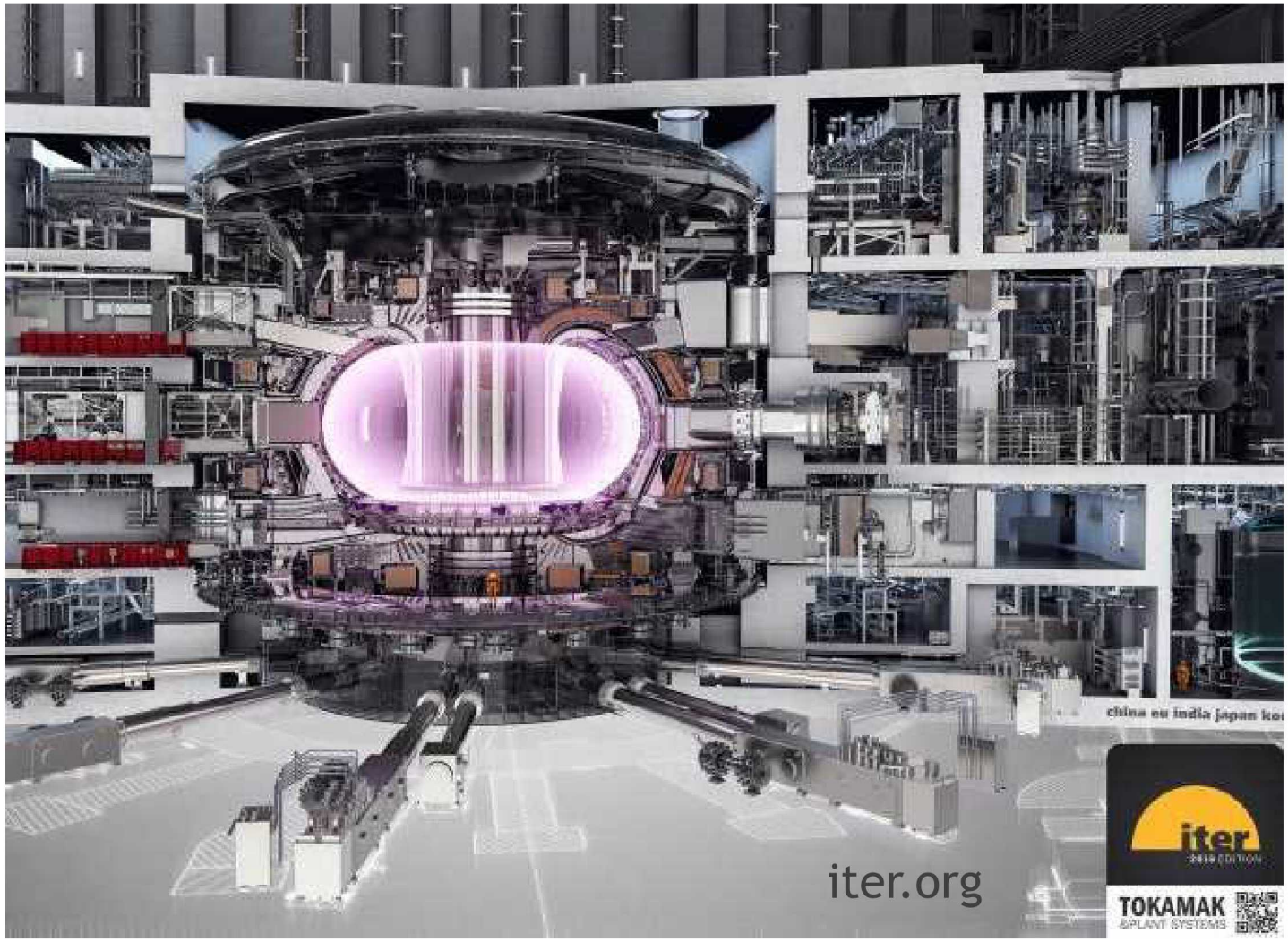
Fusion energy

"Holy grail" of energy technology

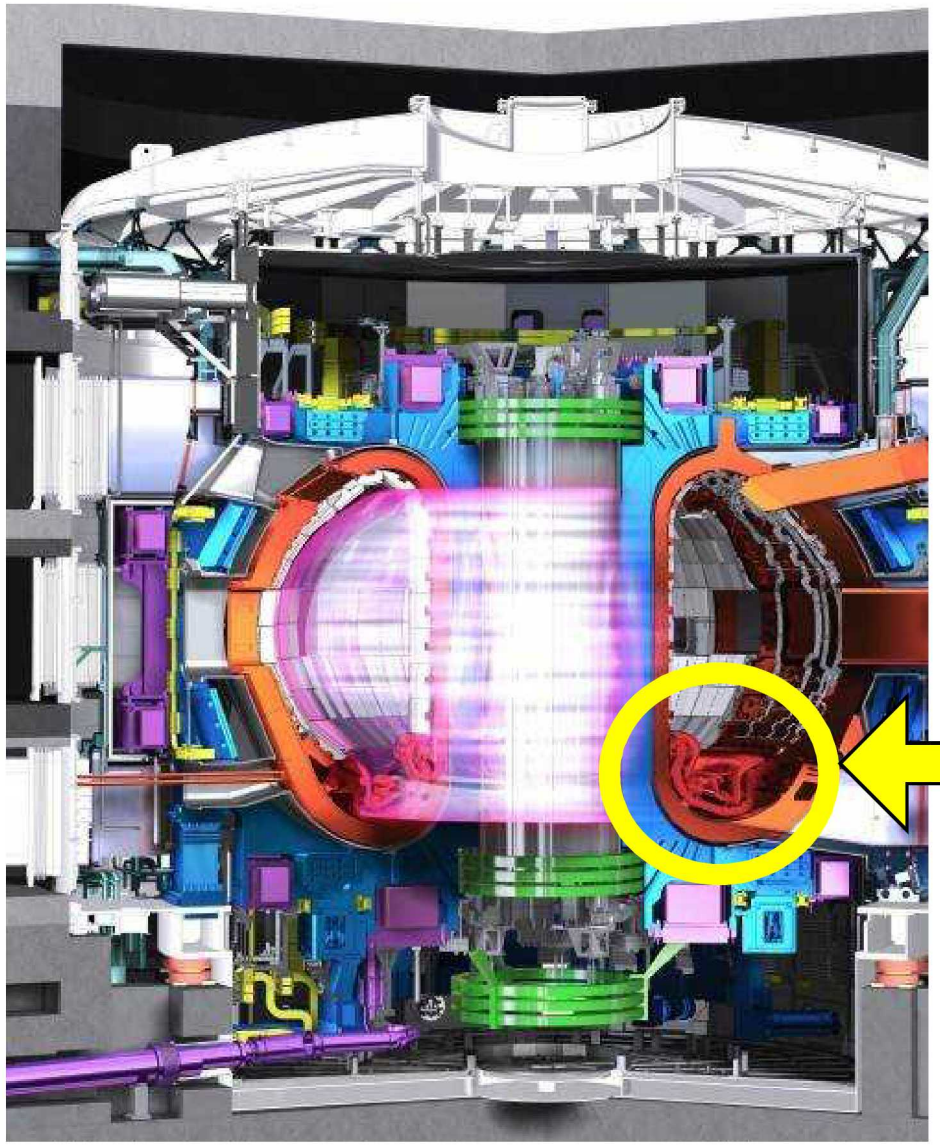
Fusion energy

- relatively clean
- sustainable & abundant
- no risk of meltdown
- really difficult

ITER—final step before a DEMO reactor



How will fusion work?



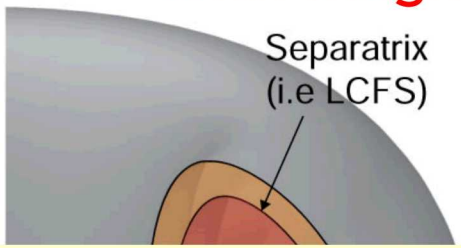
iter.org

Fusion reaction:

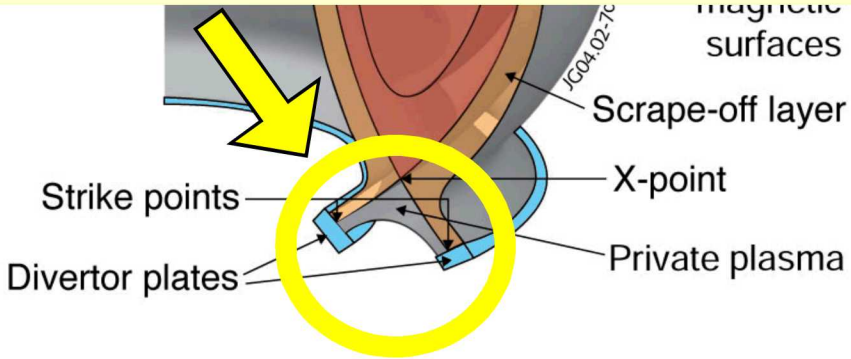
$D + T \rightarrow He + n^0$ (14.1 MeV)

requires high temperatures and plasma density

achieved by containing plasma with magnetic fields

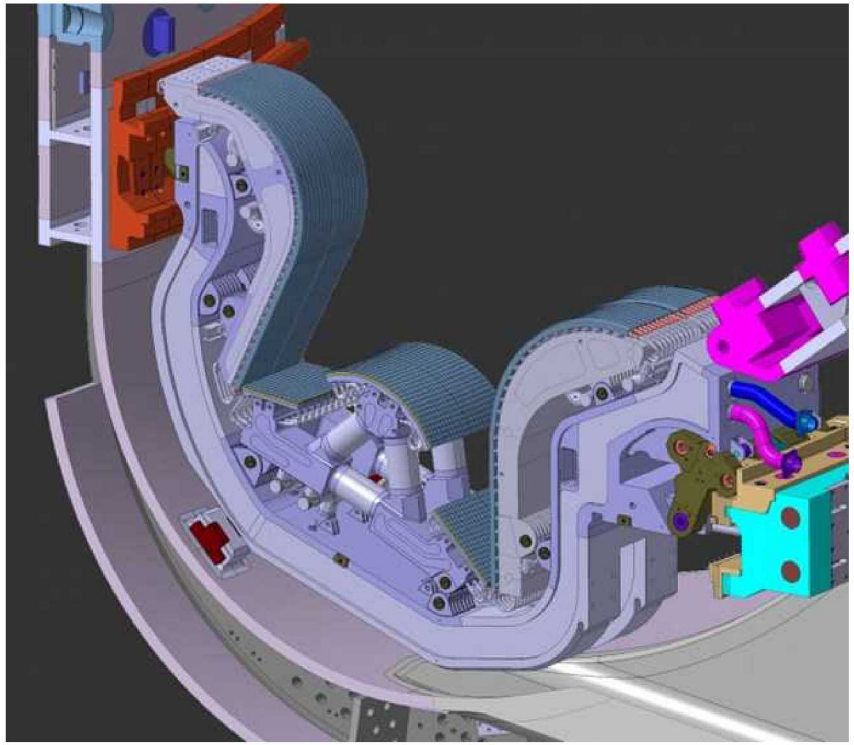


Divertor: where heat and particle flux (D, T, He, & impurities) are intentionally dumped



euro-fusion.org

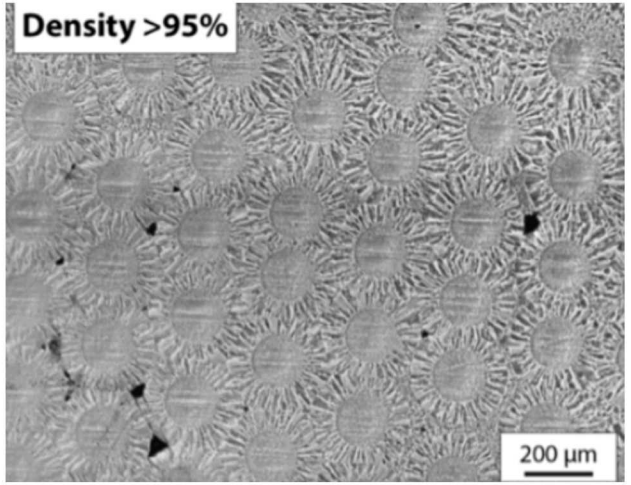
Divertor



iter.org

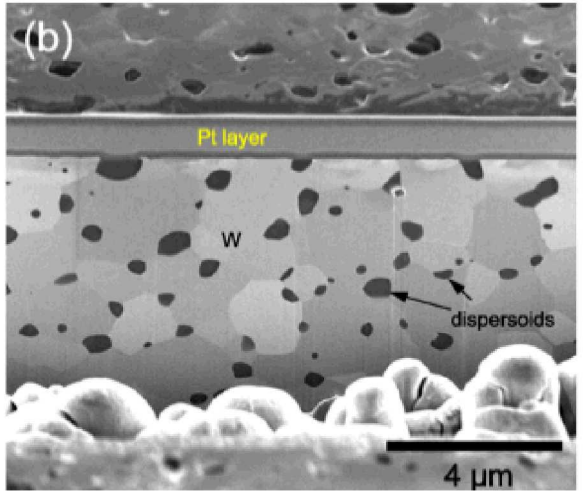
- **tungsten** is a leading candidate material
  - highest melting point
  - low sputter yield
  - high thermal conductivity
- however, polycrystalline W is likely insufficient

W-fiber reinforced W



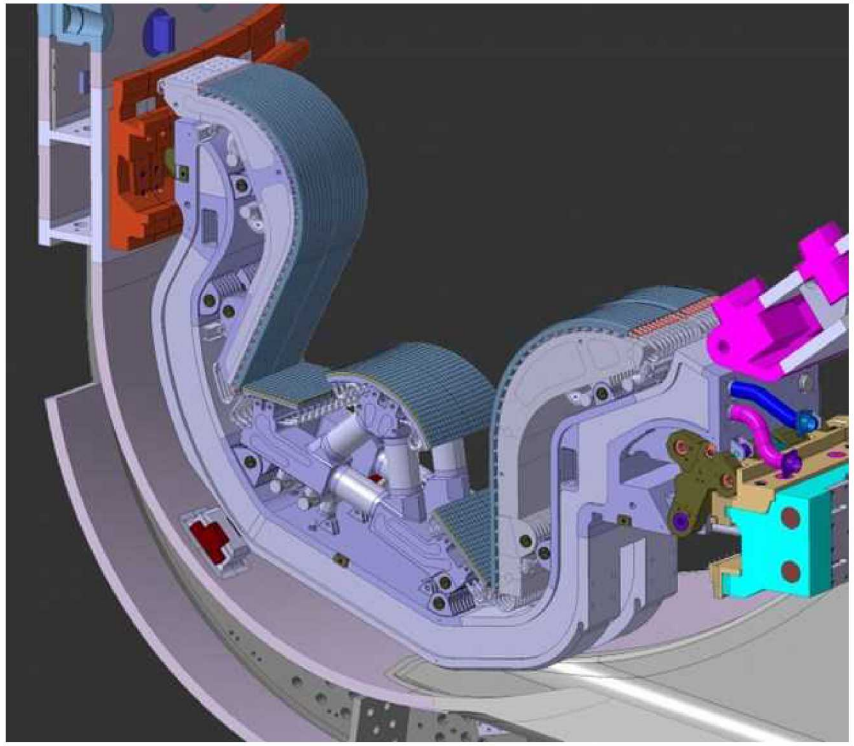
J. Coenen et al. IAEA - FEC2014

UFG-W (Ti dispersoids)



Kolasinski et al., IJRMHM, (2016).

Divertor difficulties



iter.org

Challenges for tungsten plasma-facing surfaces:

- plasma contamination (high Z)
- material degradation
  - high heat flux (melting)
  - H blistering and embrittlement
  - He plasma induced nanostructure
- tritium retention and inventory [1]
  - one 5 min shot with ITER ~ 10^5 Ci of T
  - 10 shots in 1 day = 10^6 Ci of T
  - <<1 Ci into environment—track <1 ppm!
  - serious issue! 5 μL of T_2O is lethal [2]

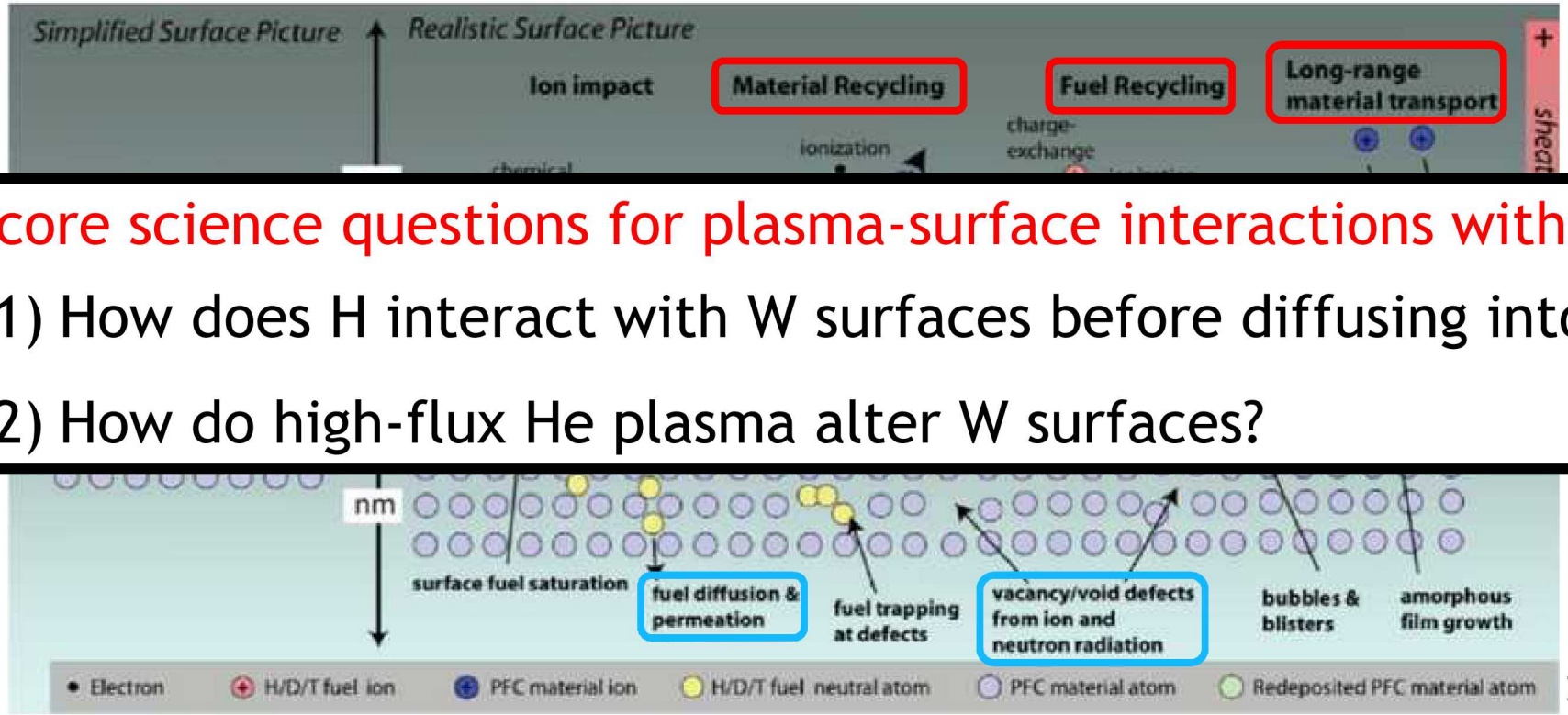
[1] T. Tanabe, J. Nucl. Mater., (2011).

[2] B. Bornstein et al., Fusion Eng. Des., (2013).

Plasma-facing surfaces in a fusion reactor

Surface physics is key for fusion!

- extremely complex, but needs to be well understood for materials development and predictive modeling (e.g. T tracking)
- plasma-surface interactions affect both the core plasma and bulk material

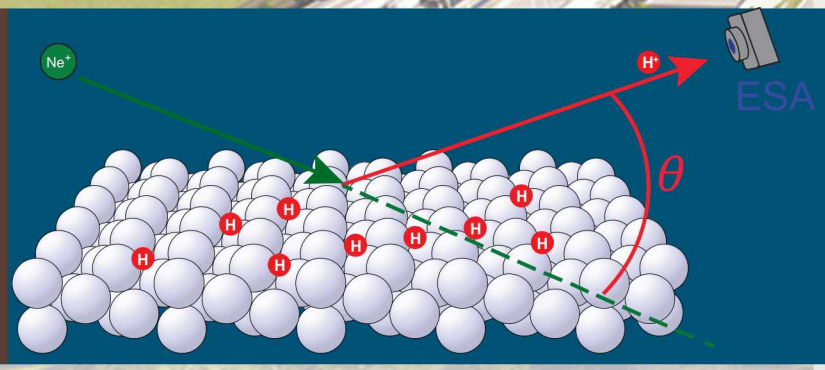


Our core science questions for plasma-surface interactions with W:

(1) How does H interact with W surfaces before diffusing into the bulk?

(2) How do high-flux He plasma alter W surfaces?

Zinckle, Fusion Sci. Tech., (2013).

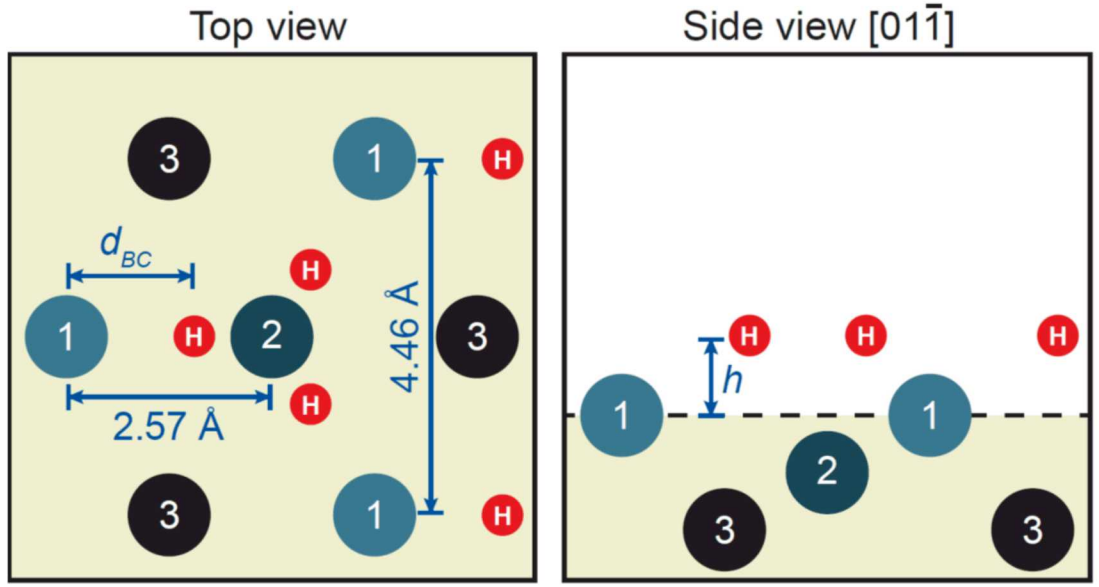


Hydrogen adsorption on W surfaces

Characterizing the W(111)+H(ads) system

H adsorption on W(111)

Bond centered (BC) site on W(111) predicted using density functional theory (DFT) by Zack Bergstrom and Brian Wirth at University of Tennessee



1.5 Å ≤ d_{BC} ≤ 1.7 Å

0.95 Å ≤ h ≤ 1.10 Å

Experimentally validate DFT results:

DFT provides inputs for larger scale models

e.g. interatomic potentials for molecular dynamics (MD) simulations

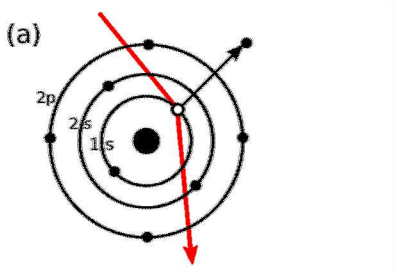
Z. Bergstrom et al., J. Phys.: Condens. Matter, (2019).

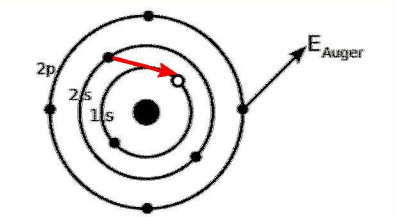
Detection of surface hydrogen is challenging

Not many experimental techniques are directly sensitive to surface hydrogen

AES

Auger electron spec.



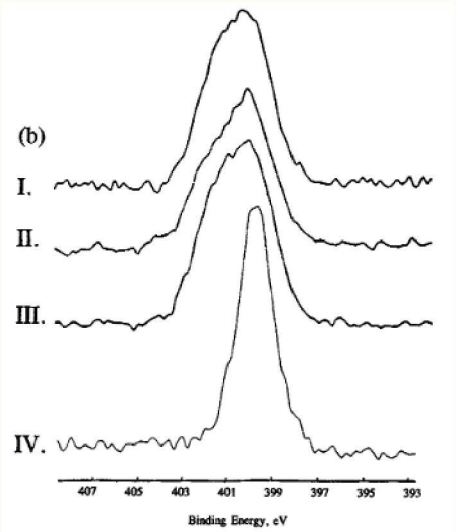


no auger electrons for H

XPS

X-ray photoelectron spec.

Shifts in N 1*s* peaks possibly due to H bonding



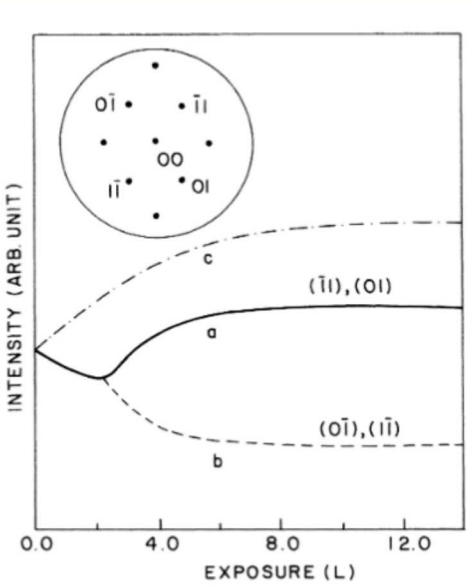
Kerber et al., J. Vacuum Sci. Tech., (1996).

small shifts in peaks due to H binding

LEED

Low energy electron diffraction

Reconstruction of W(110) due to H adsorption



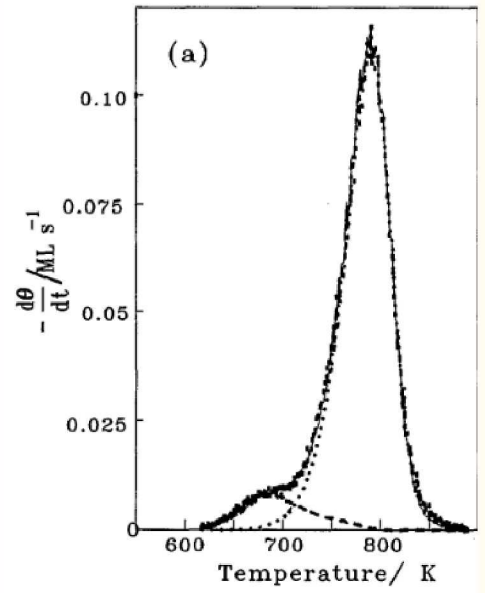
Chung et al., PRL, (1986).

indirect H detection from reconstruction

TPD

Temp. programmed desorption

Desorption of D from Si

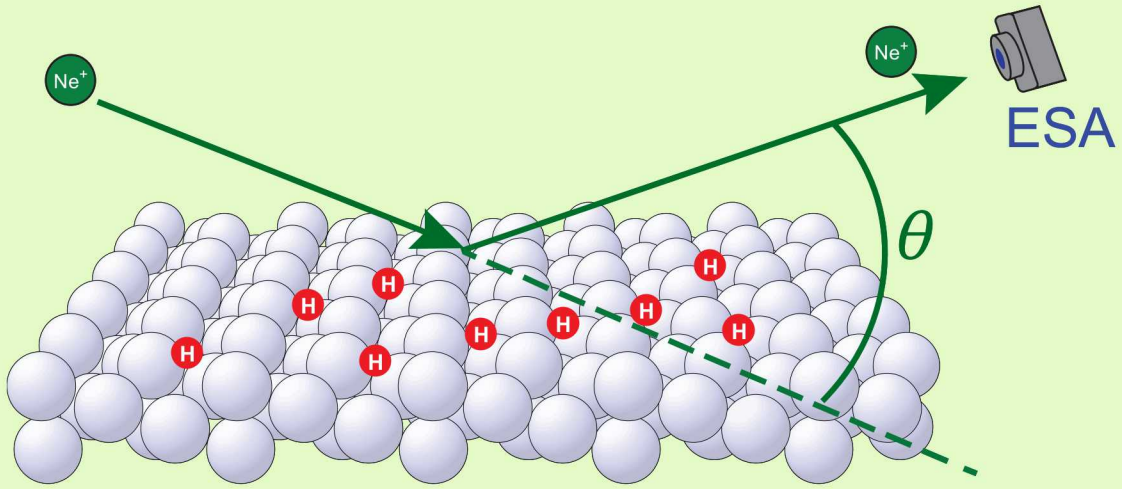


Flowers et al., J. Chem. Phys. (1993).

H amount and activation energies, not locations

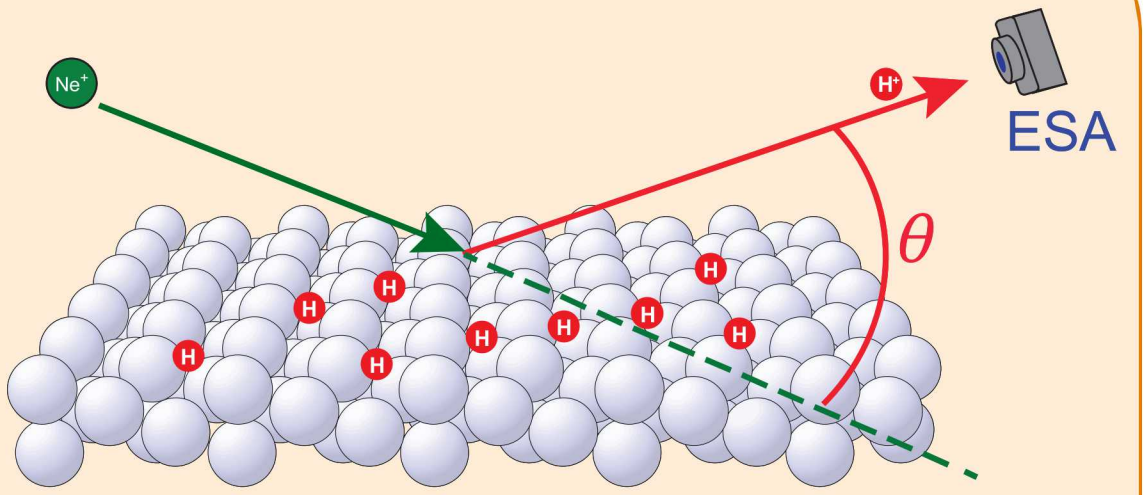
LEIS and DRS

Low energy ion scattering (LEIS)



$$\frac{E}{E_0} = \left(\frac{\cos\theta \pm \sqrt{\mu^2 - \sin^2\theta}}{1+\mu} \right)^2$$

Direct recoil spectroscopy (DRS)

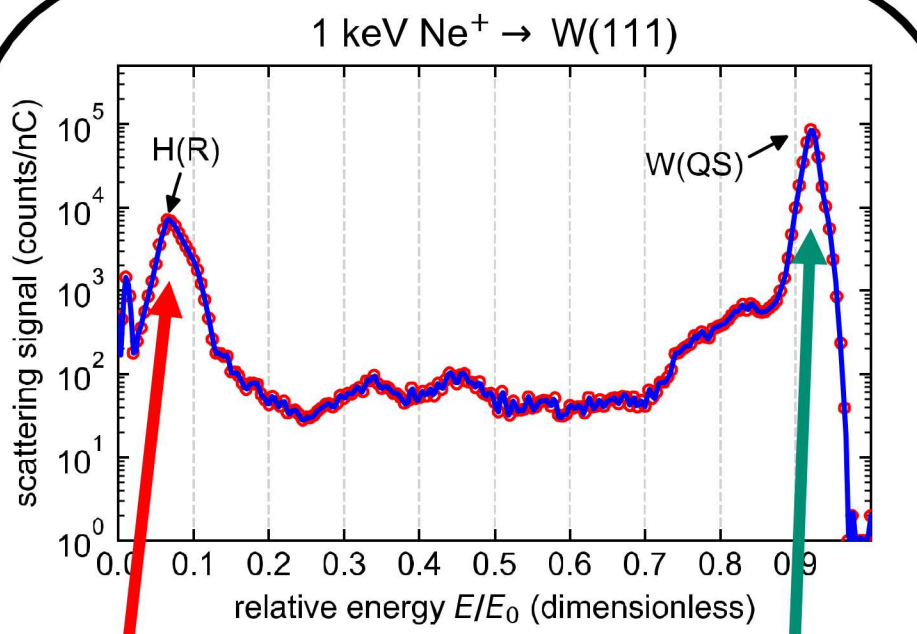


$$\frac{E}{E_0} = \frac{4\mu}{(1+\mu)^2}\cos^2\theta$$

- both techniques can be performed simultaneously
- energy of detected ion depends only on μ and θ

$$\mu = \frac{m_T}{m_P}$$

Why DRS and LEIS?



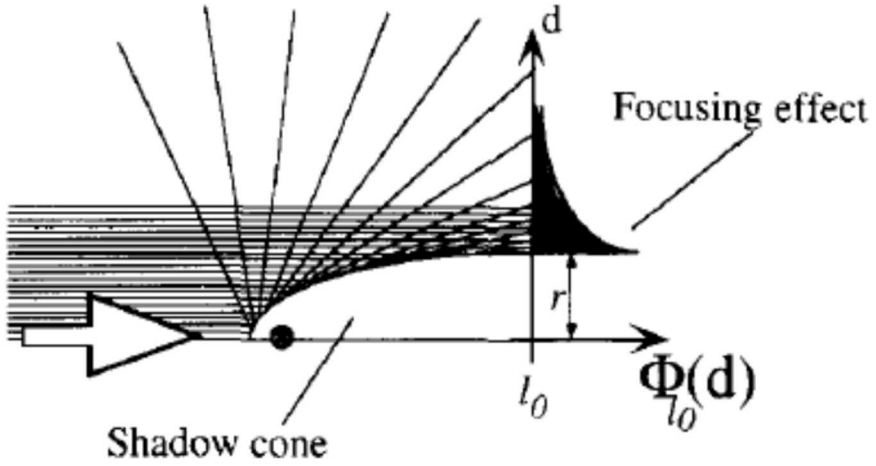
$$\frac{E}{E_0} = \frac{4\mu}{(1+\mu)^2}\cos^2\theta$$

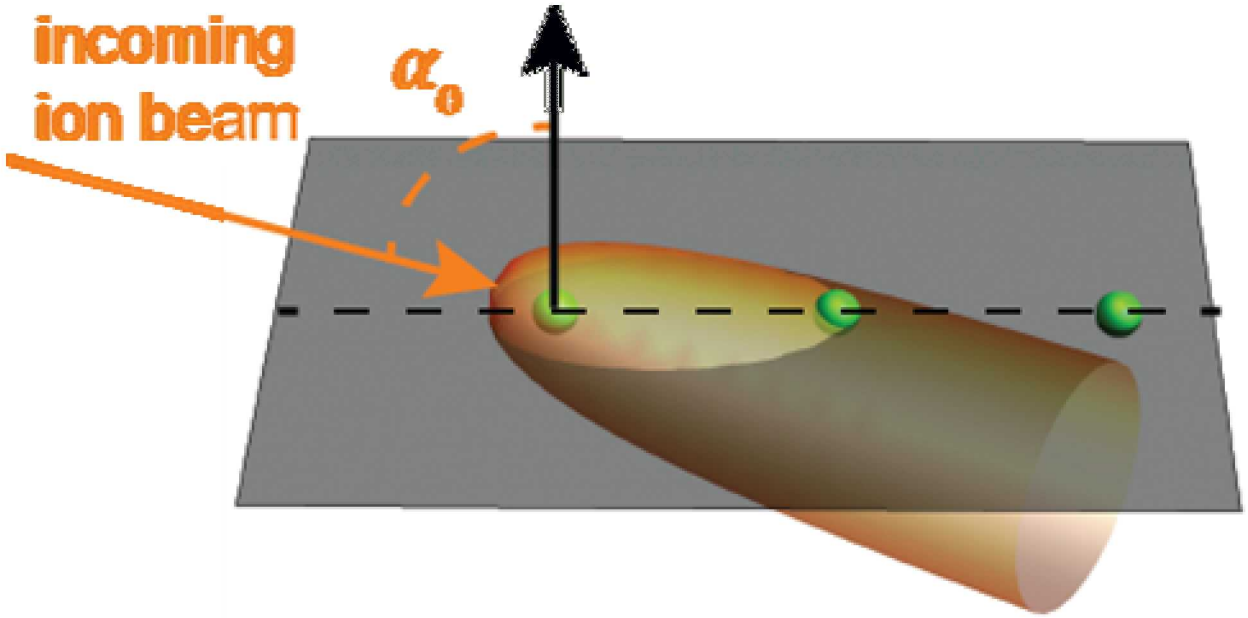
$$\frac{E}{E_0} = \left(\frac{\cos\theta \pm \sqrt{\mu^2 - \sin^2\theta}}{1+\mu}\right)^2$$

Advantages of LEIS & DRS

1) direct detection of hydrogen on surface
2) studies for insulating materials are possible
3) surface specificity: ultra-thin depth profiling (monolayer sensitivity)
4) structural information can be obtained with more complex measurements and modeling

Shadow cones





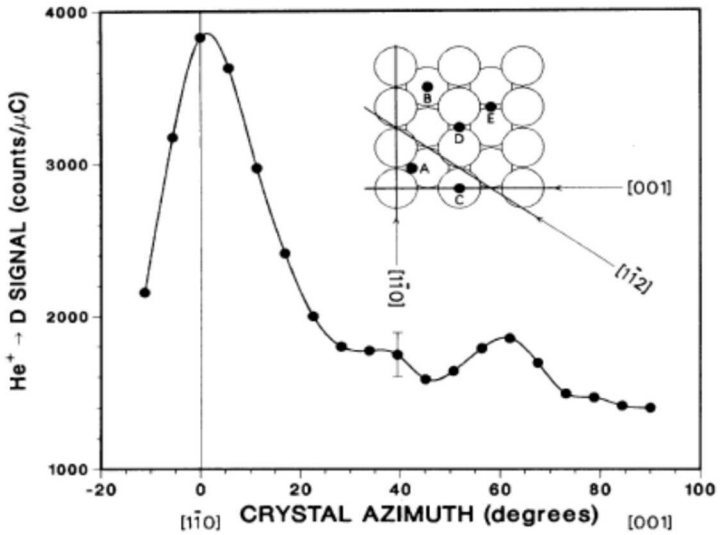
[3] Agostino et al., Surf. Sci. **384,** (1997).

- Shadow cone arises from ion focusing
- Enhanced scattering or recoil signal when cone coincides with neighboring atom

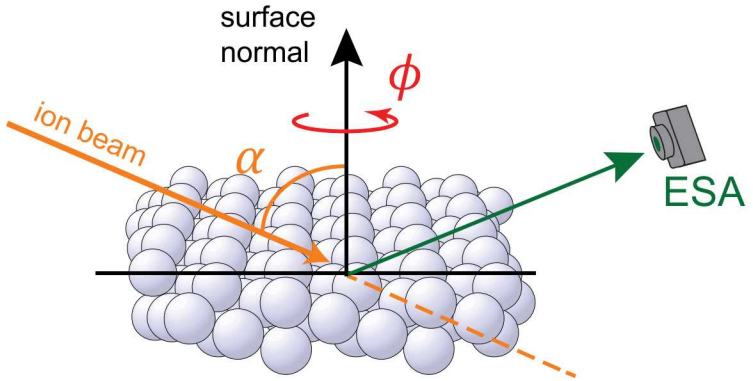
Early study to find H on surfaces—shadow cone analysis

LEIS to detect D on Pd surface

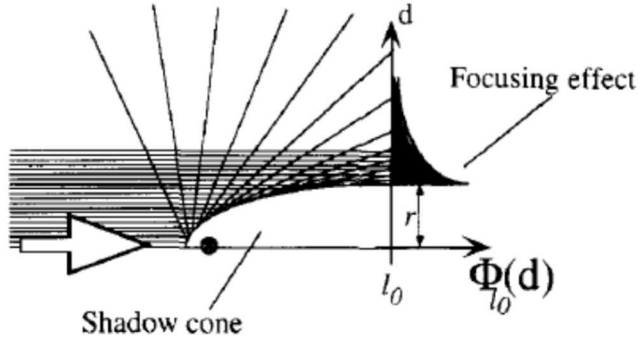
Bastasz et al., Phys. Rev. Lett. **63**, (1989).



D scattering signal, varying only ϕ

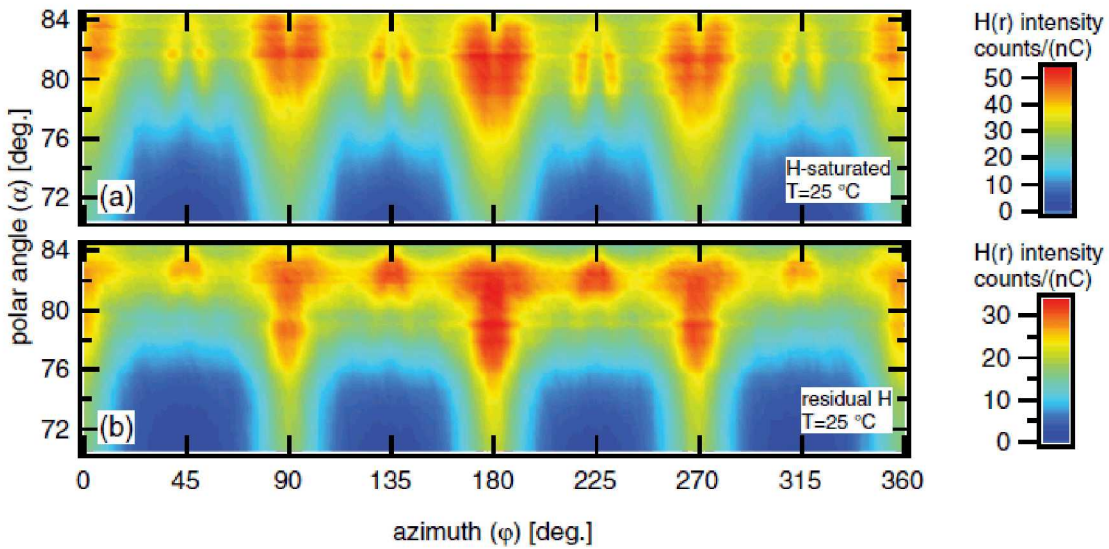


- based on D being hidden by Pd-atom shadow cones
- unable to fully determine binding site
- only works for D, not H

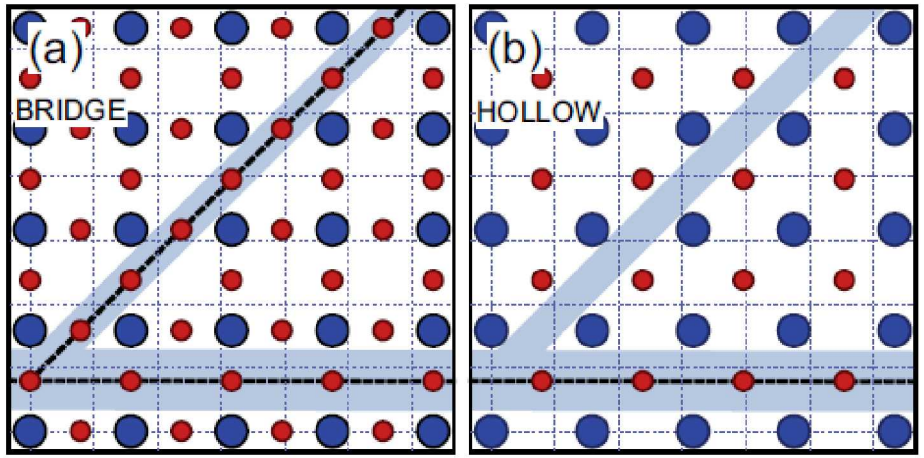


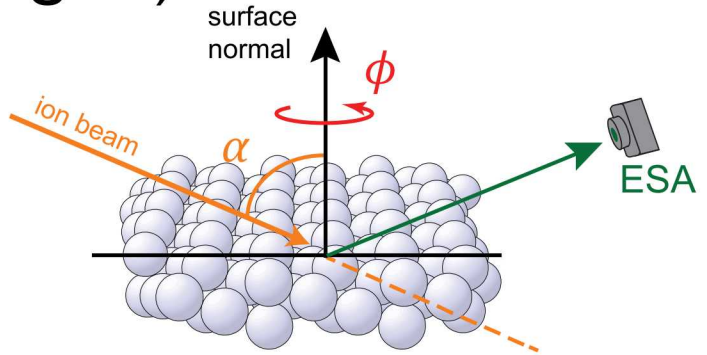
[3] Agostino et al., Surf. Sci. **384,** (1997).

Channeling with multi-angle maps (varying both angles)



H within channel ➔ recoil peak

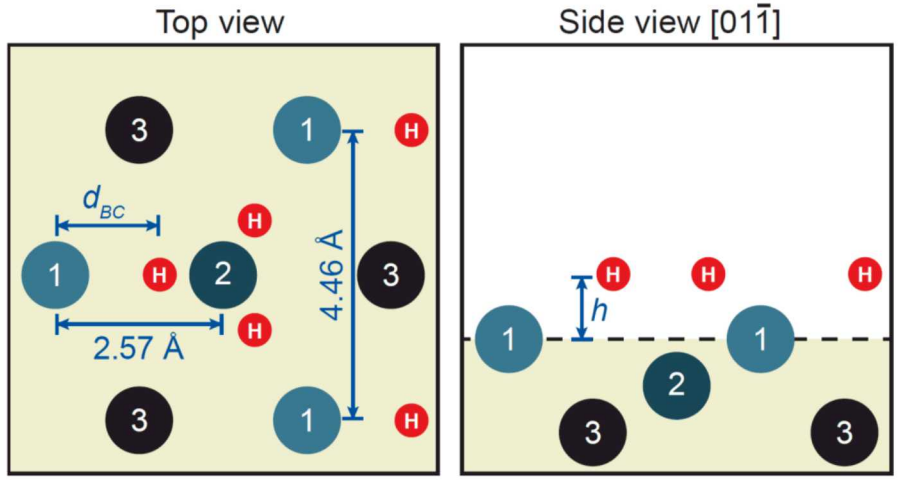




[4] Kolasinski et al., PRB **85,** (2012).

- maps provide information on ion channeling
- detection of adsorbates not limited to near-surface
- only considers scattering from top monolayer and adsorbates
- does not identify complex binding geometries

Bond centered site on W(111)



1.5 Å ≤ d_{BC} ≤ 1.7 Å 0.95 Å ≤ h ≤ 1.10 Å

Previously described methods are insufficient:

1. complex adsorbate binding geometry
2. corrugated surface of W(111) leads to scattering by sub-surface atoms

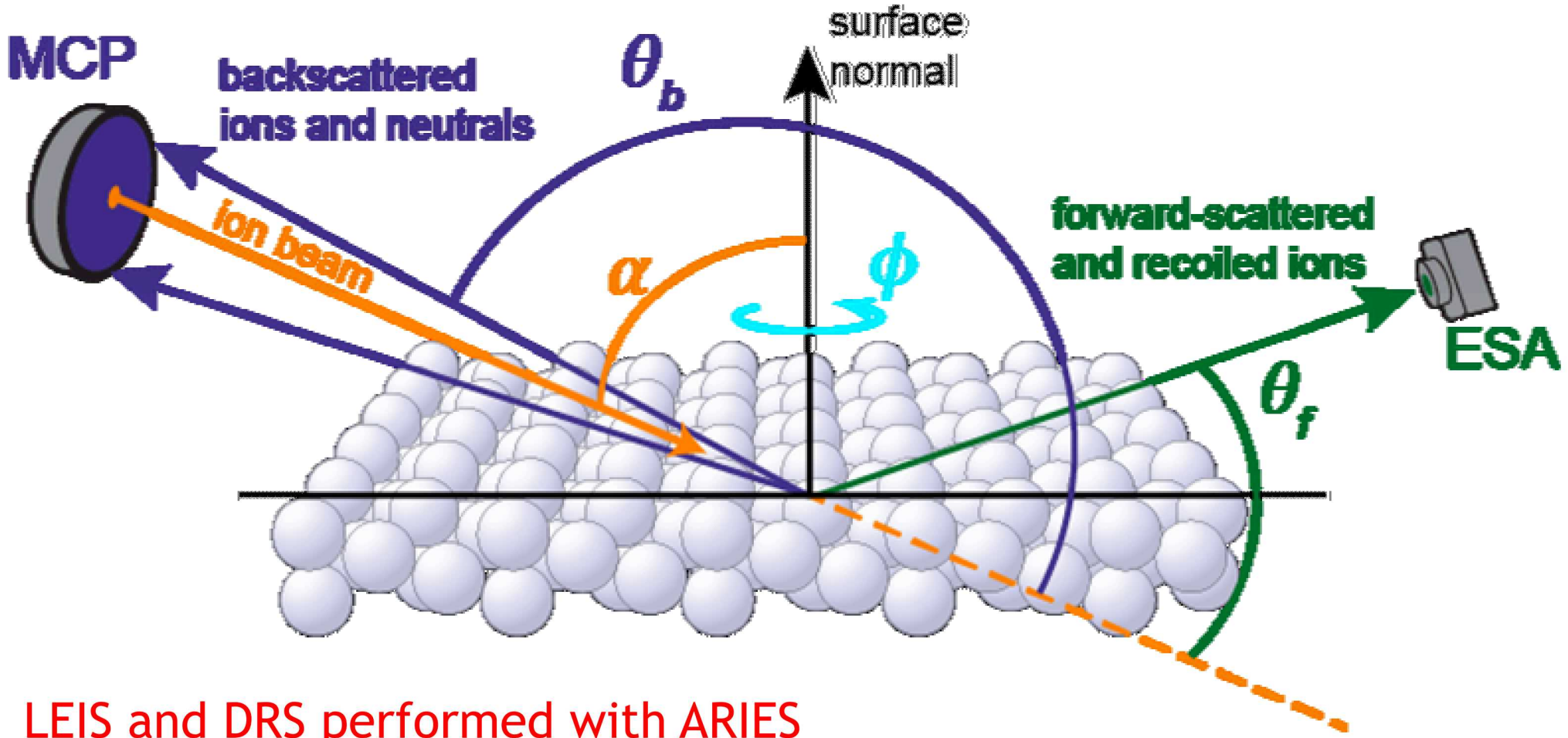
Characterization of W(111)+H(ads) required the following advances:

1. extend shadow cone analysis for multi-layer scattering
2. perform more extensive MD simulations to determine H binding site
3. develop a more complete ion channeling model to describe recoil maps

C.-S. Wong, J. Whaley, Z. Bergstrom, B. Wirth, and R. Kolasinski, *submitted to* **Phys. Rev. B.**

Multi-layer scattering from W(111) substrate

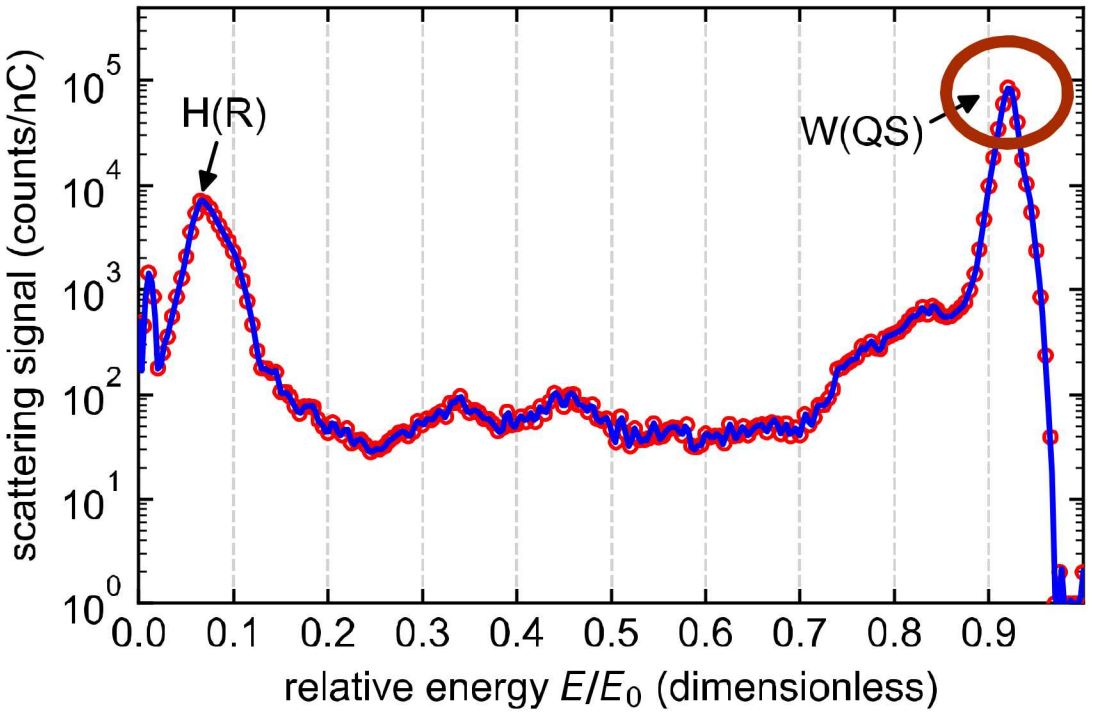
ARIES: Angle-Resolved Ion Energy Spectrometer

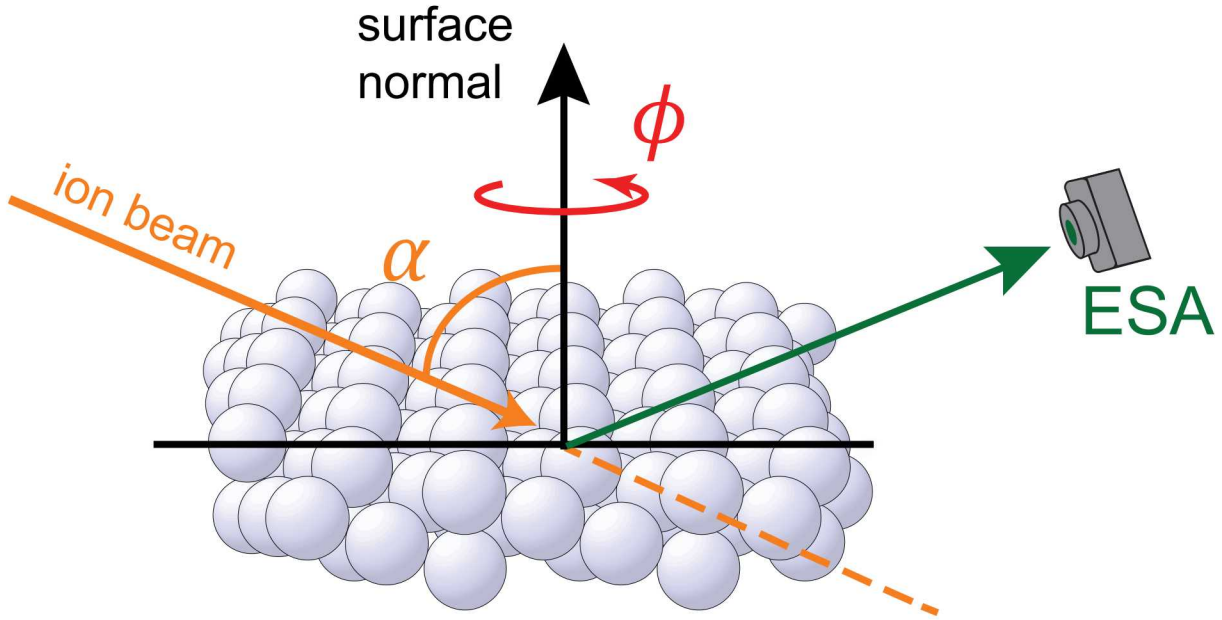


- LEIS and DRS performed with ARIES
- can also be configured for backscattering measurements

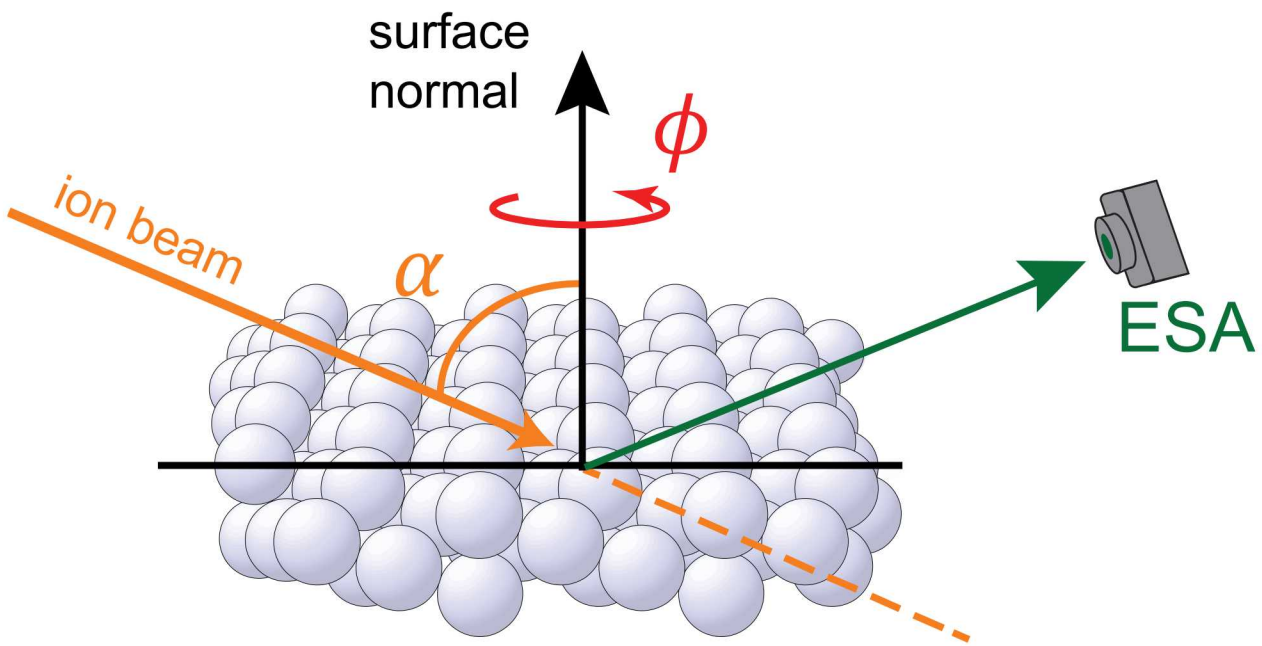
Constructing multi-angle scattering maps with ARIES

track counts of scattered Ne^+ while varying angles α and ϕ





Multi-angle scattering maps for W(QS)



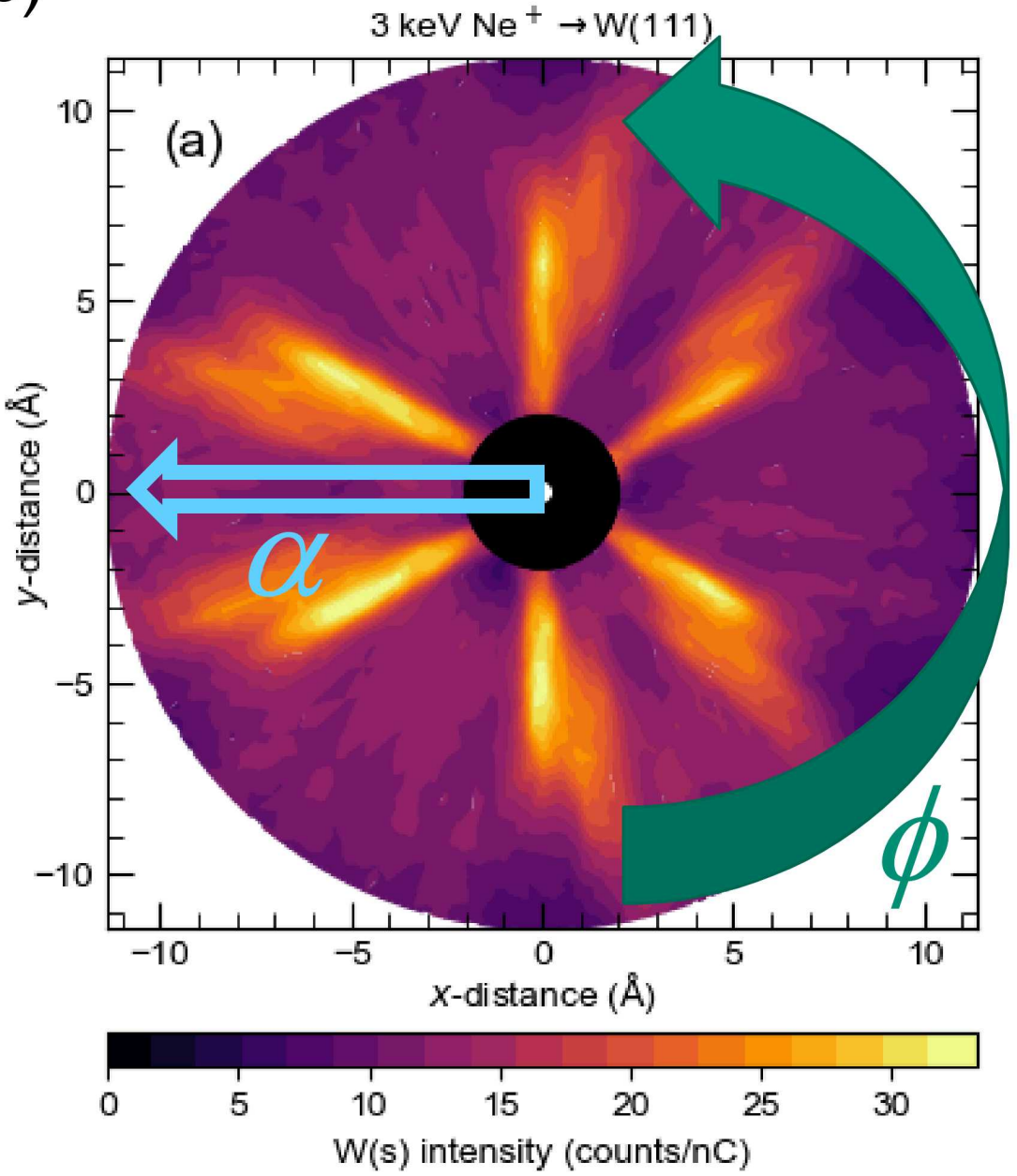
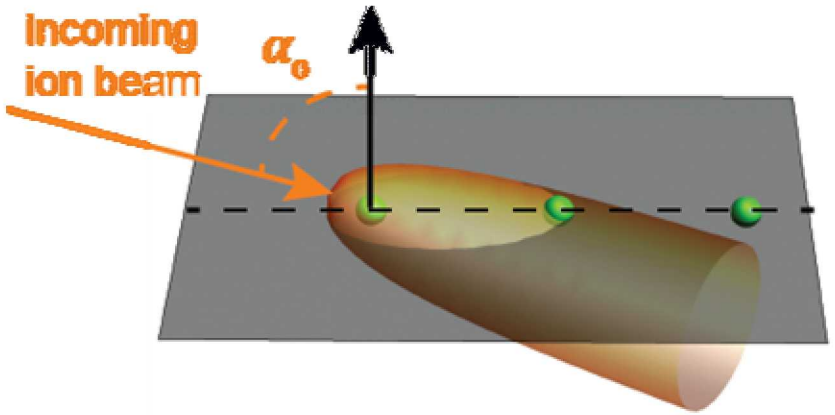
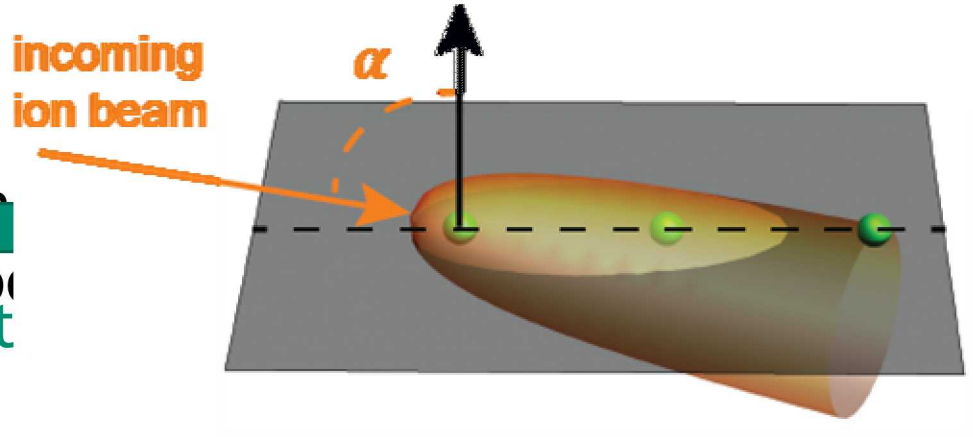
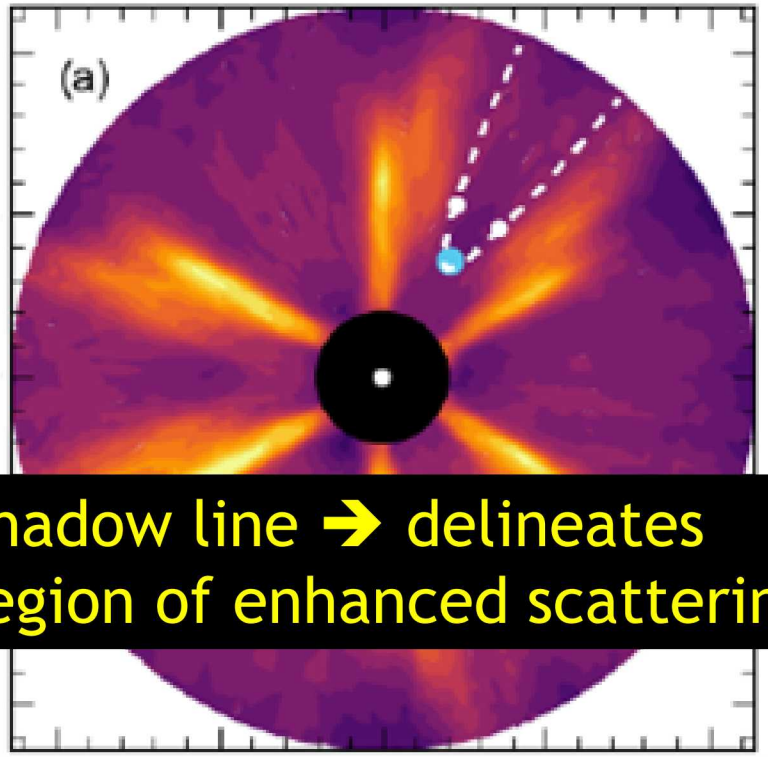


Illustration of shadow line analysis



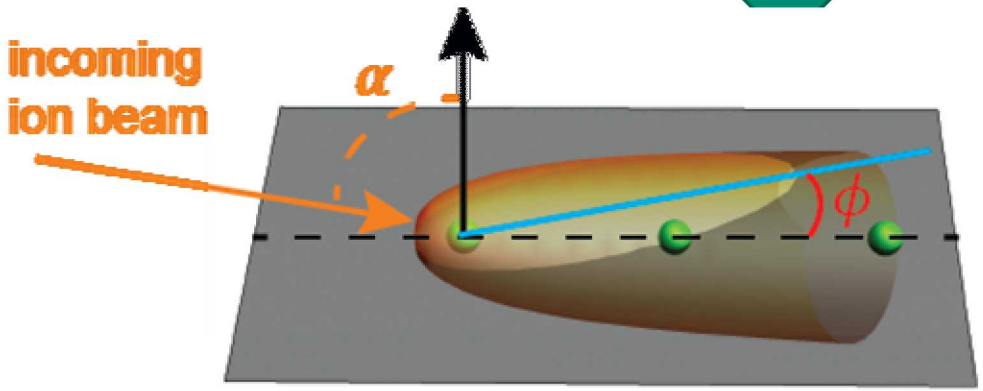
L[redacted]
coincides with neighb
shadow cone overshoot
neighbor for larger α





Shadow line ➔ delineates region of enhanced scattering

edge of cone realigned by ϕ rotation

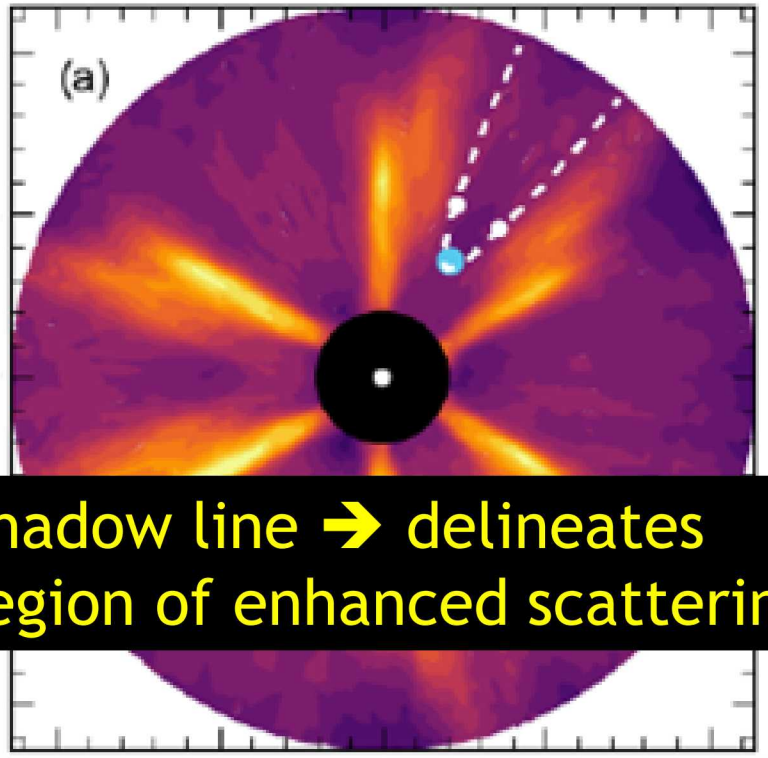


Agostino et al., Surf. Sci. **384,** (1997).

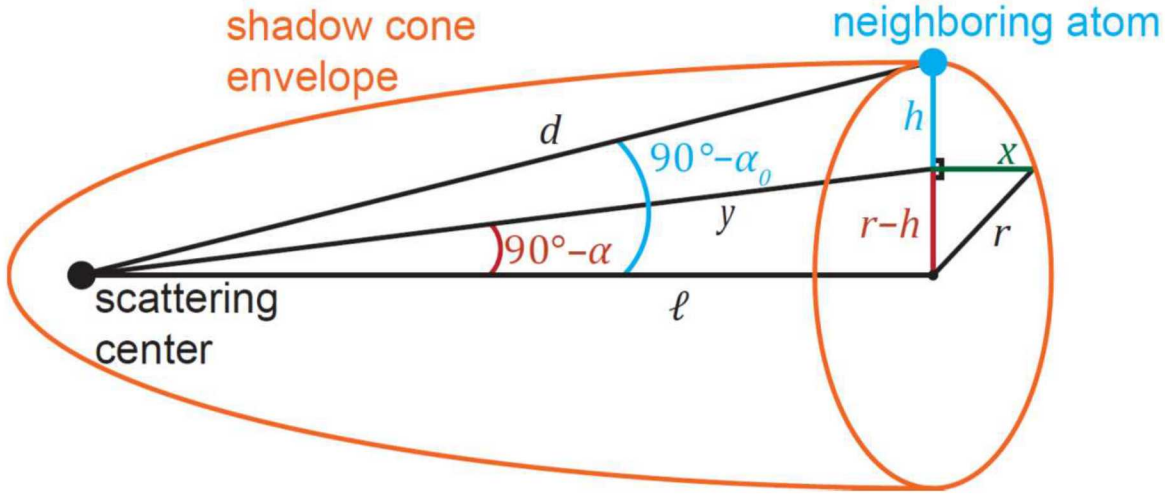
Shadow lines—analytic description

- In the literature, shadow lines were calculated numerically
- I showed that shadow lines can be determined analytically, based on geometrical arguments:

$$\phi_{rot} = \arctan\left[\cot(\alpha_0)\sqrt{1-\frac{\cos^2(\alpha)}{\cos^2(\alpha_0)}}\right]$$

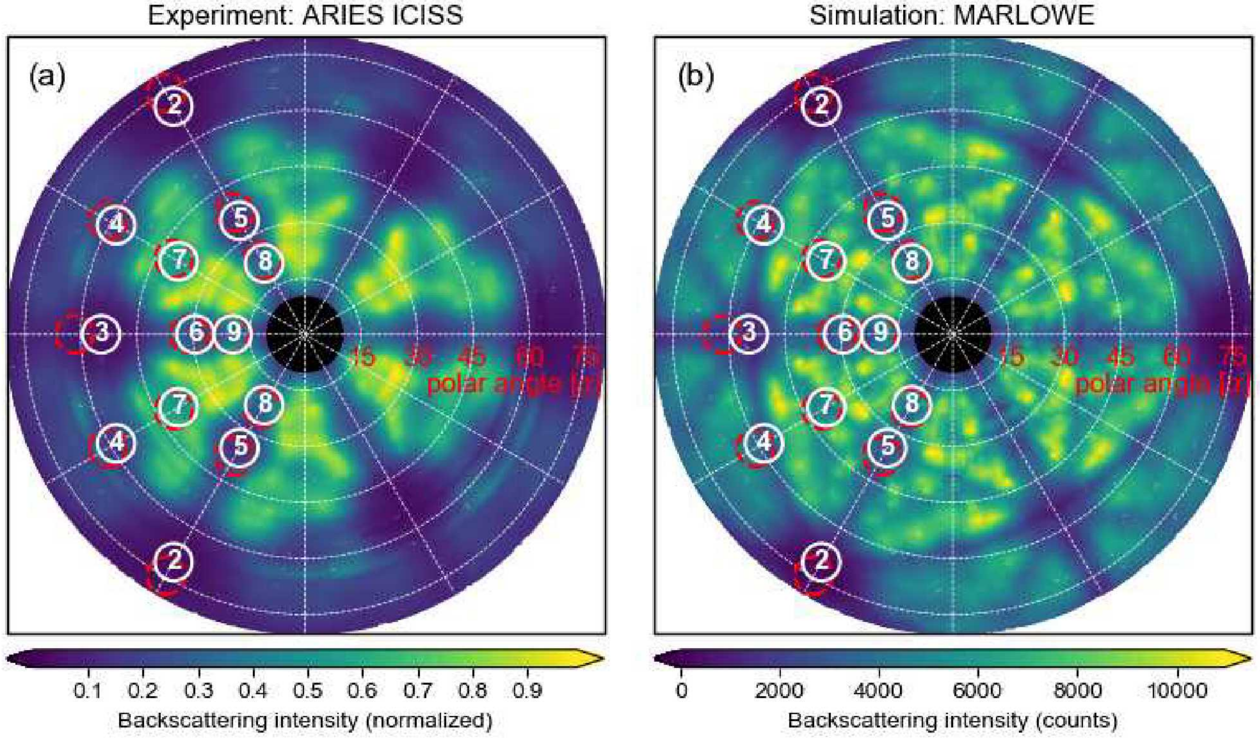


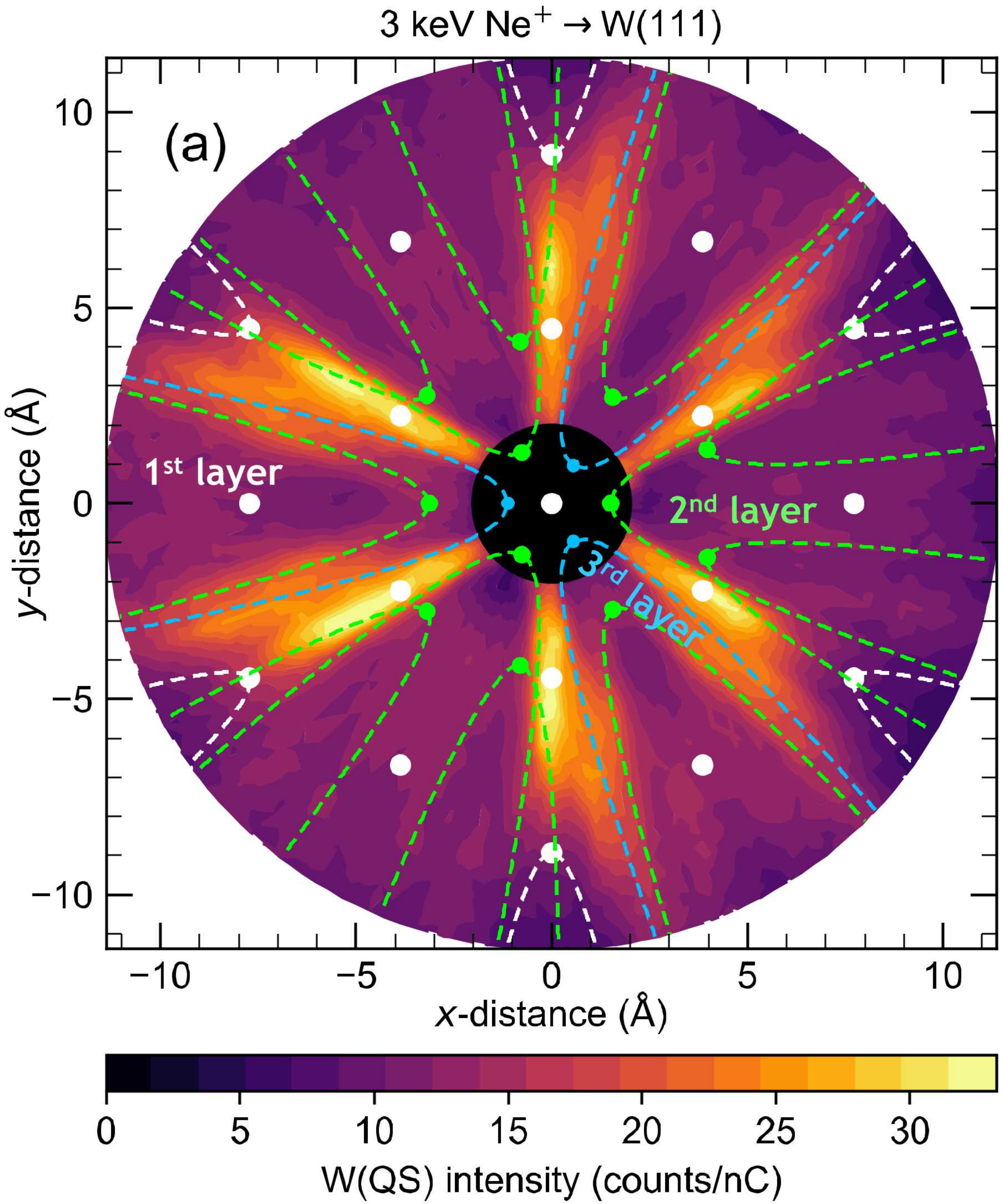
Shadow line ➔ delineates region of enhanced scattering



Shadow lines for three W layers

- Getting closer… but can the scattering signal near the center be explained?
- Crystalline orientation confirmed with ICISS backscattering maps

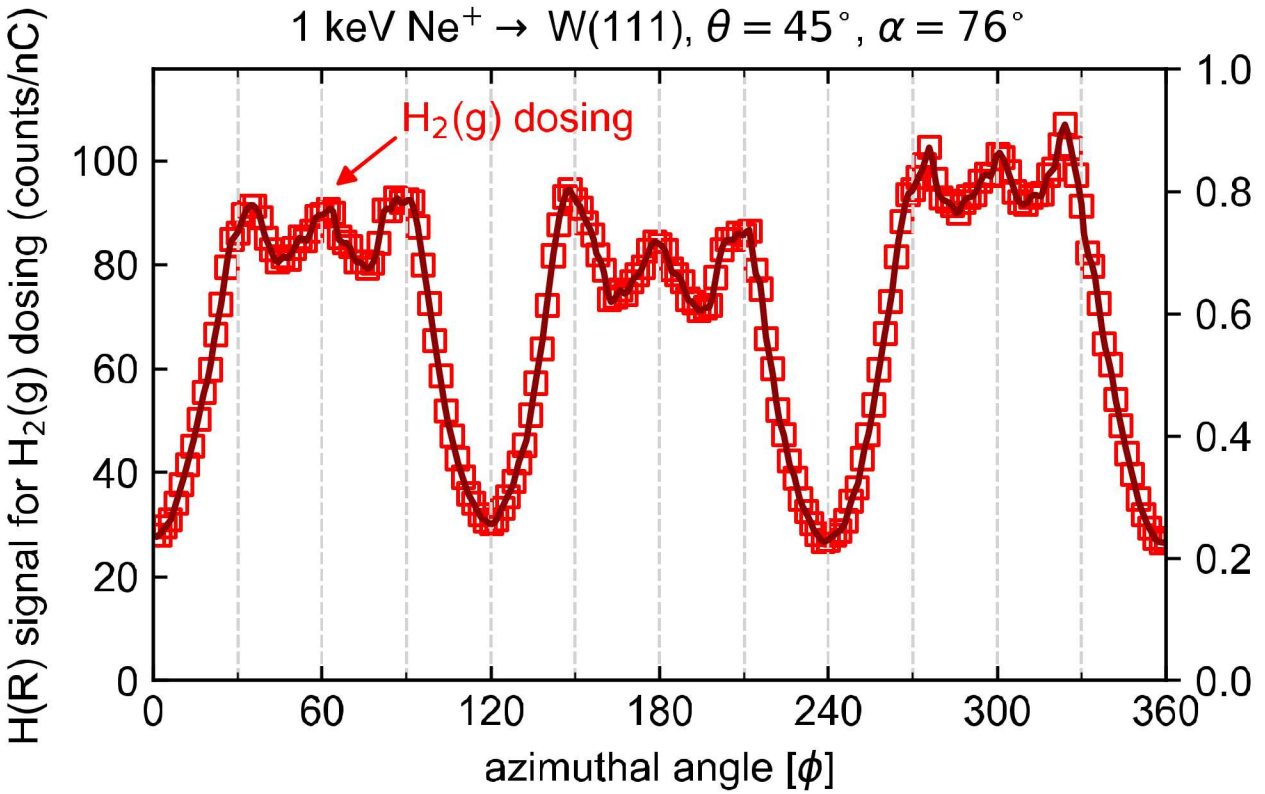


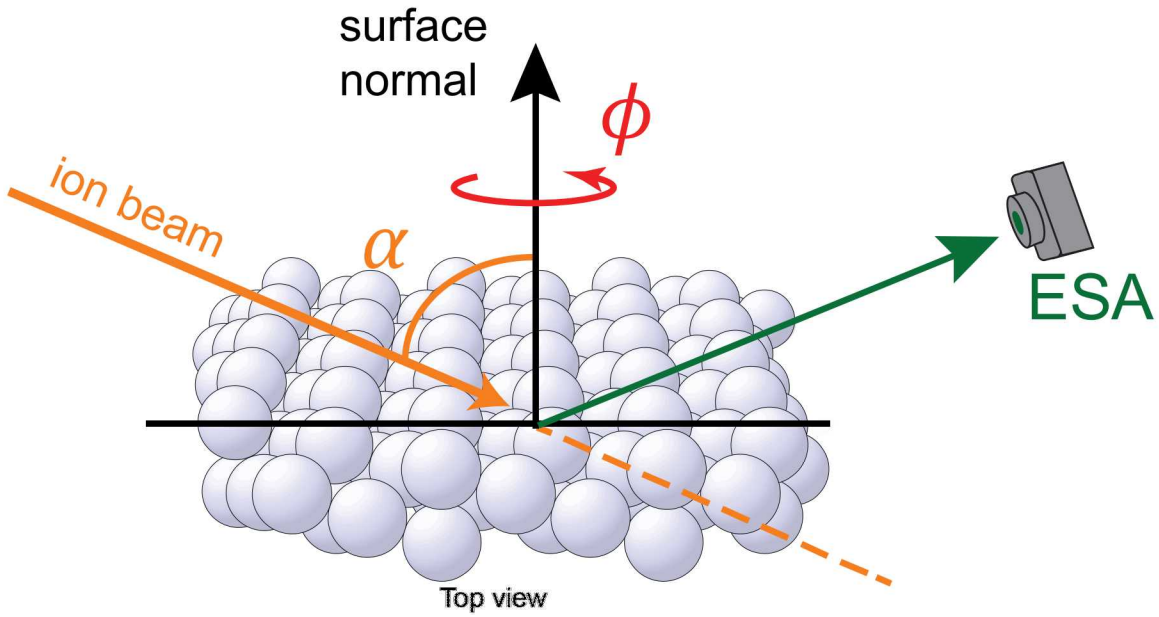


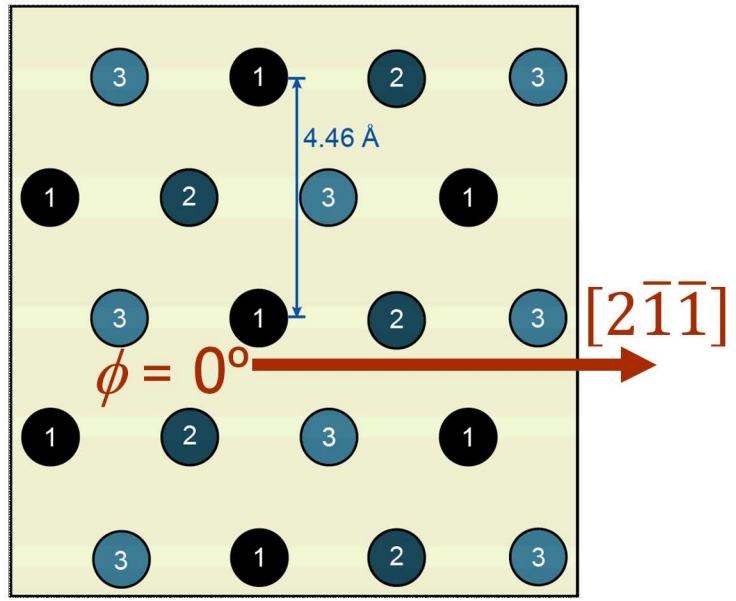
Determination of H adsorption sites on W(111):

modeling experimental data with MD simulations

Obtaining H recoil measurement at a single α

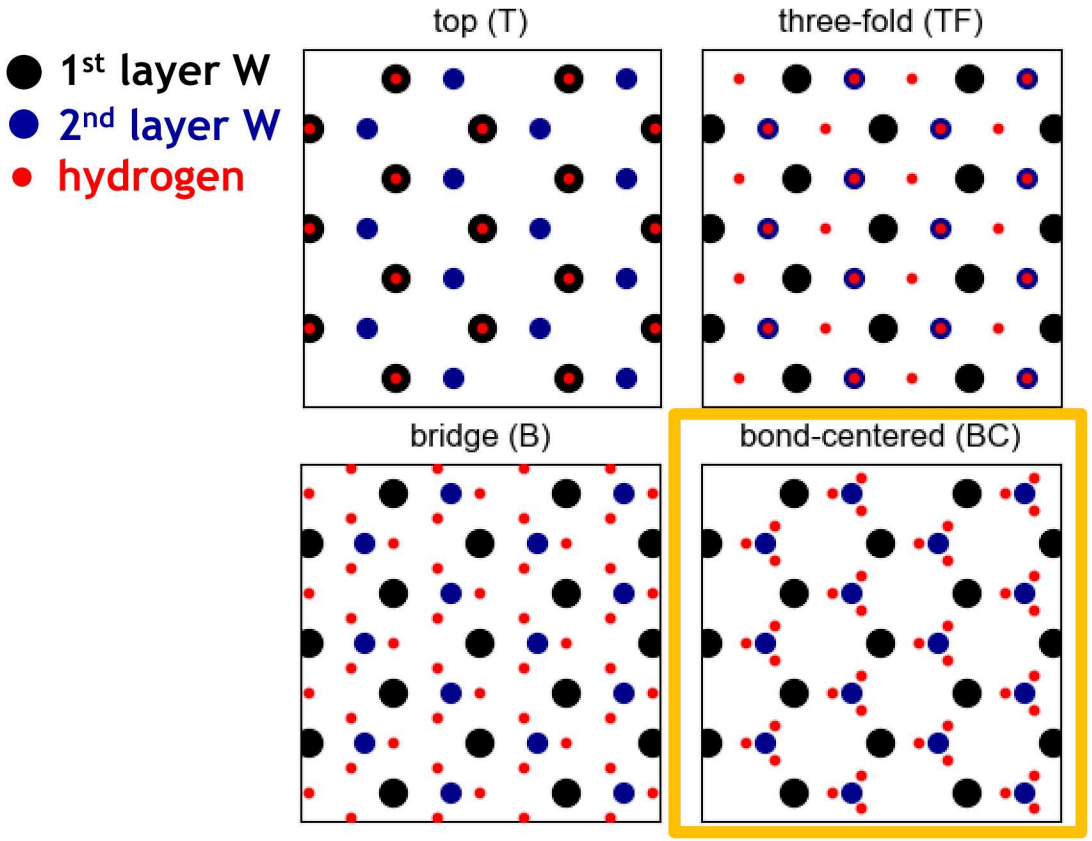




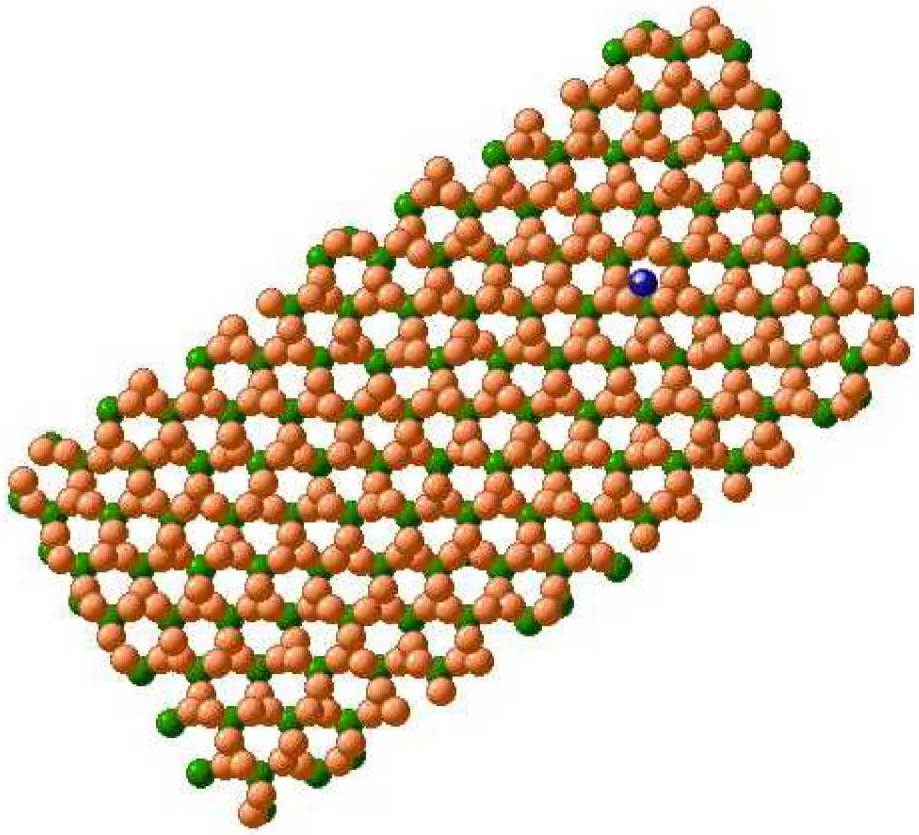


Molecular dynamics (MD) simulations with Kalypso [5]

Simulations performed for the DFT predicted BC site as well as 3 other high symmetry sites for comparison



DFT prediction



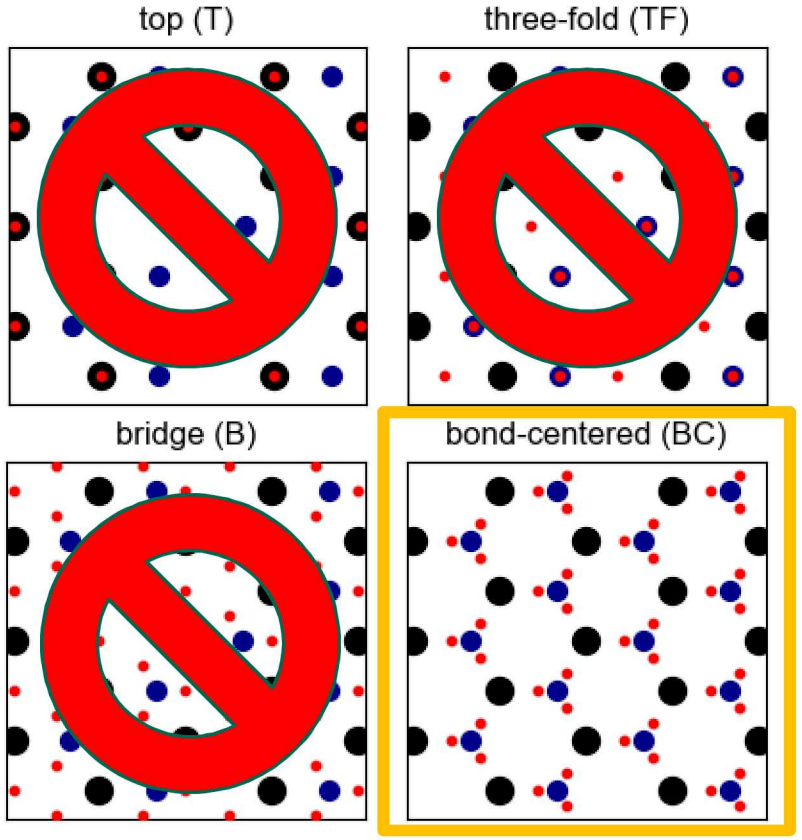
[5] Karolewski, Nucl. Instrum. Methods Phys. Res. B **230,** (2005).

Modeling H(R) with molecular dynamics (MD) simulations

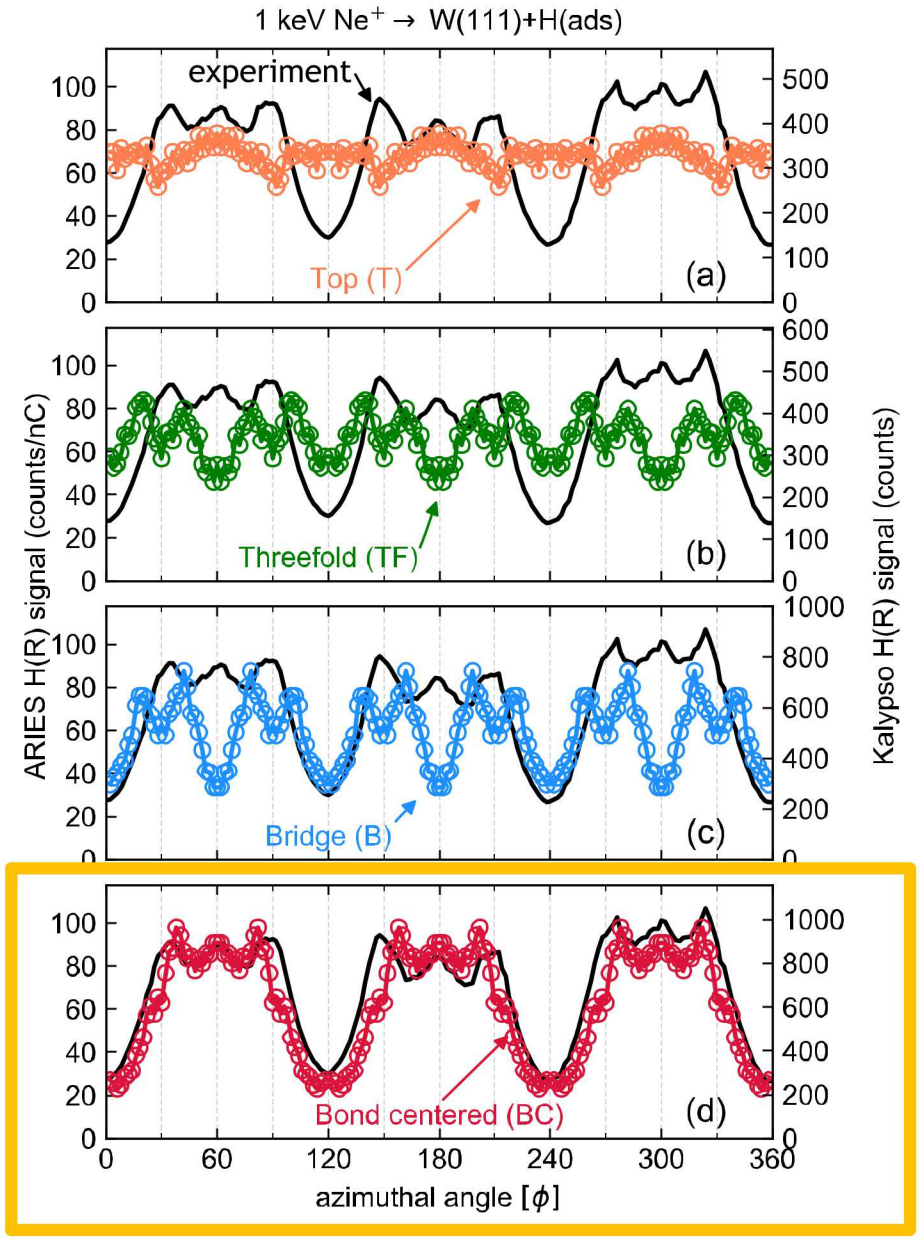
physics included	assumptions made
saturated H coverage on W substrate	elastic collisions—universal ZBL potential
surface relaxation of W substrate*	only include projectile—target interactions
vibrational displacements of W & H*	stationary target atoms
only count recoiled H with final trajectory and energy that corresponds to detector	damage to target was not tracked

*DFT calculations performed by collaborators at U. Tenn

MD simulation results compared to experimental H(R)



DFT prediction



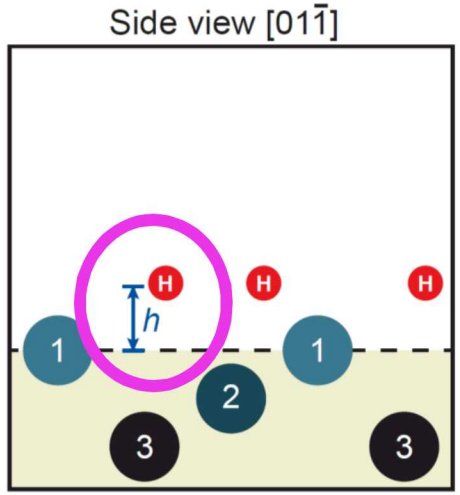
Constraining adsorbate height and position

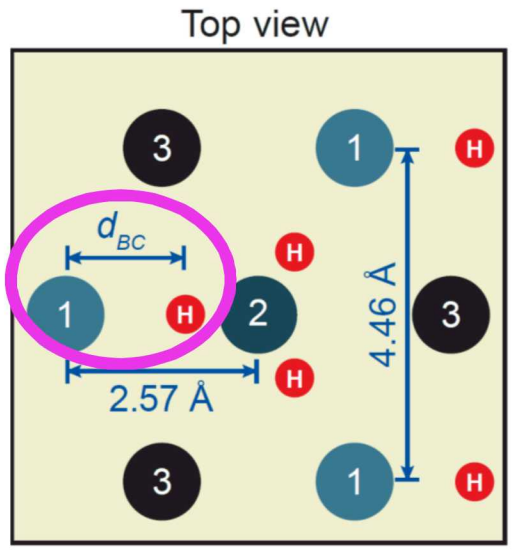
h = 1.0 ± 0.1 Å

DFT prediction:
0.95 Å ≤ h ≤ 1.10 Å

d_{BC} = 1.6 ± 0.1 Å

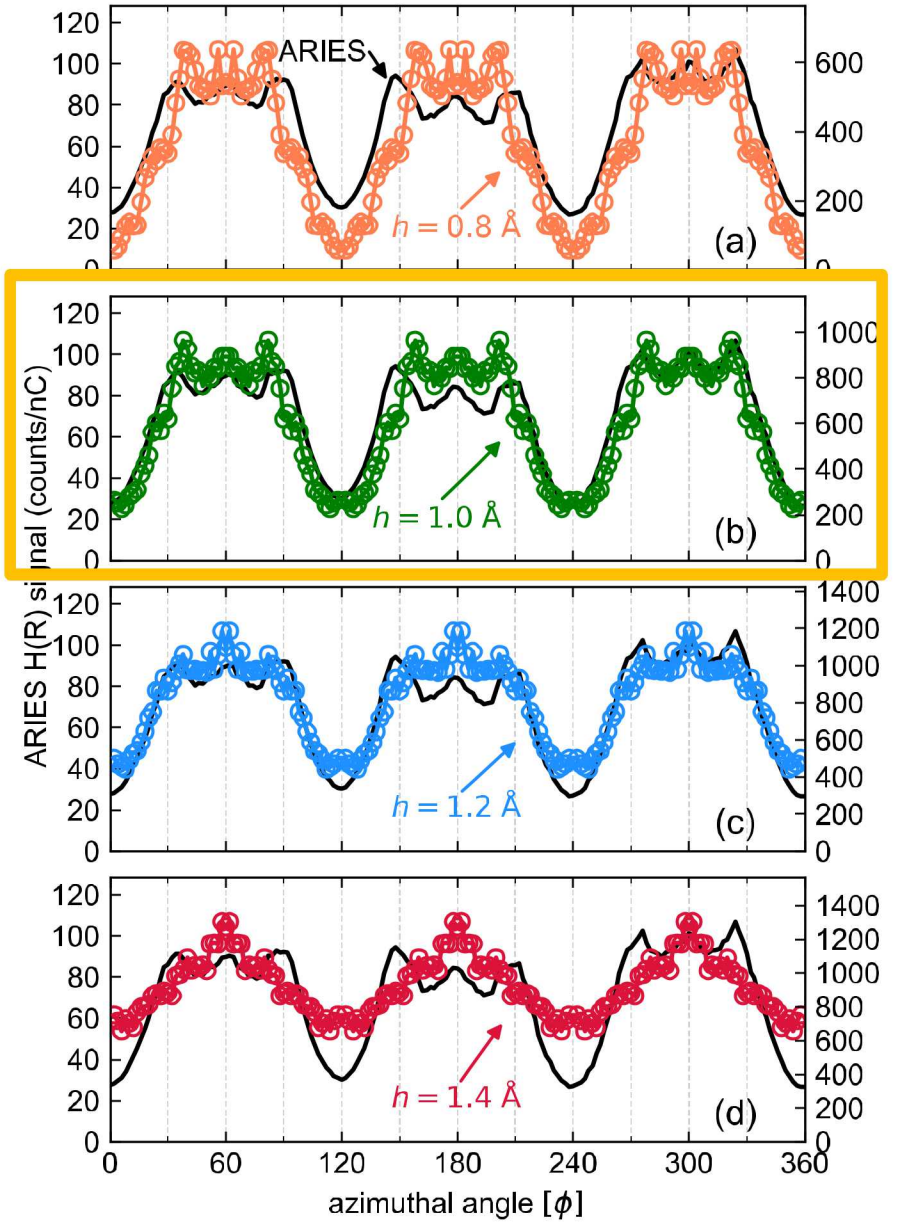
DFT prediction:
1.5 Å ≤ d_{BC} ≤ 1.7 Å





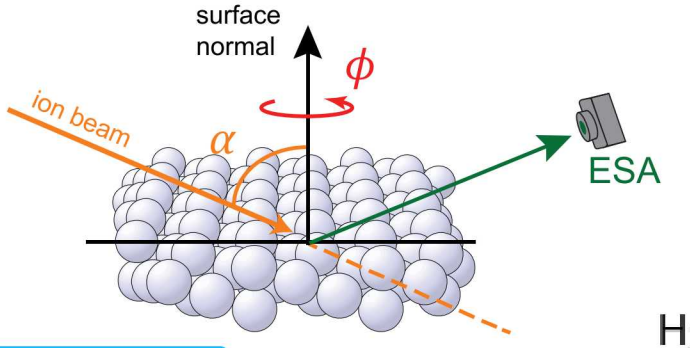
DFT prediction

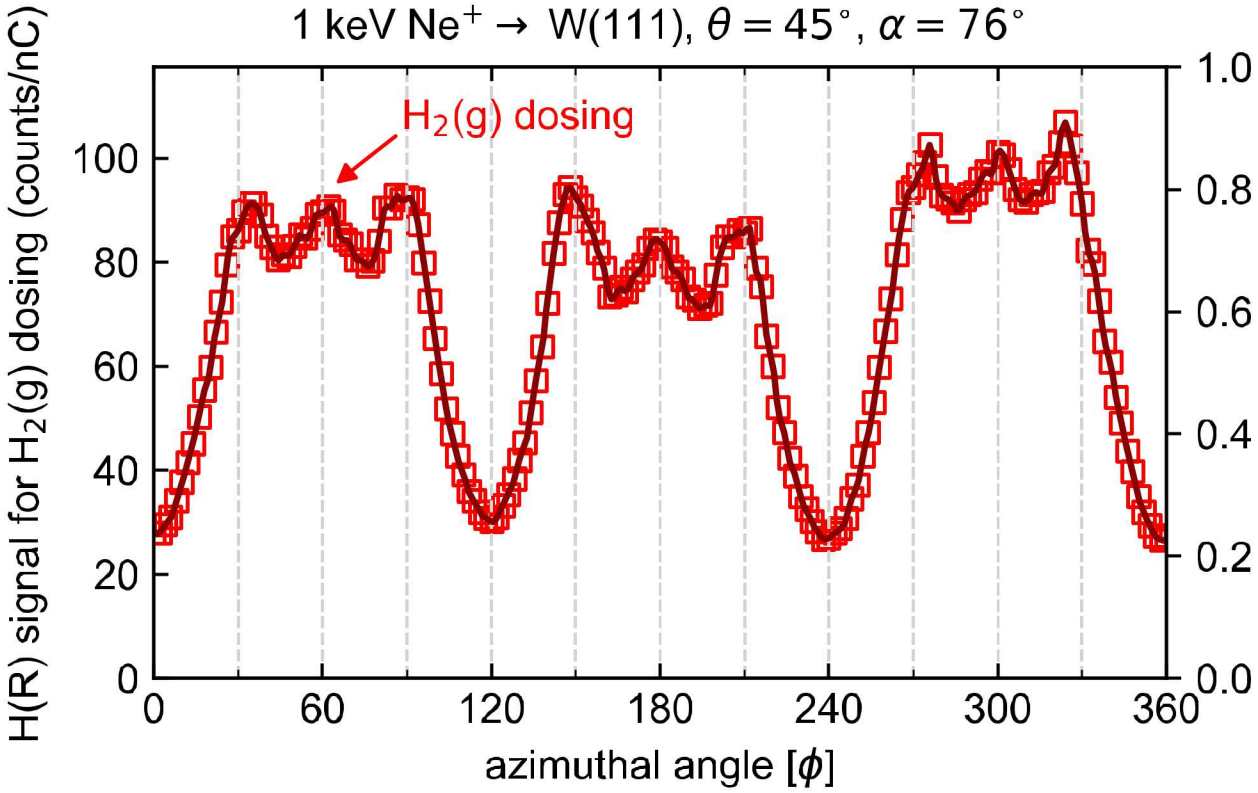
varying h

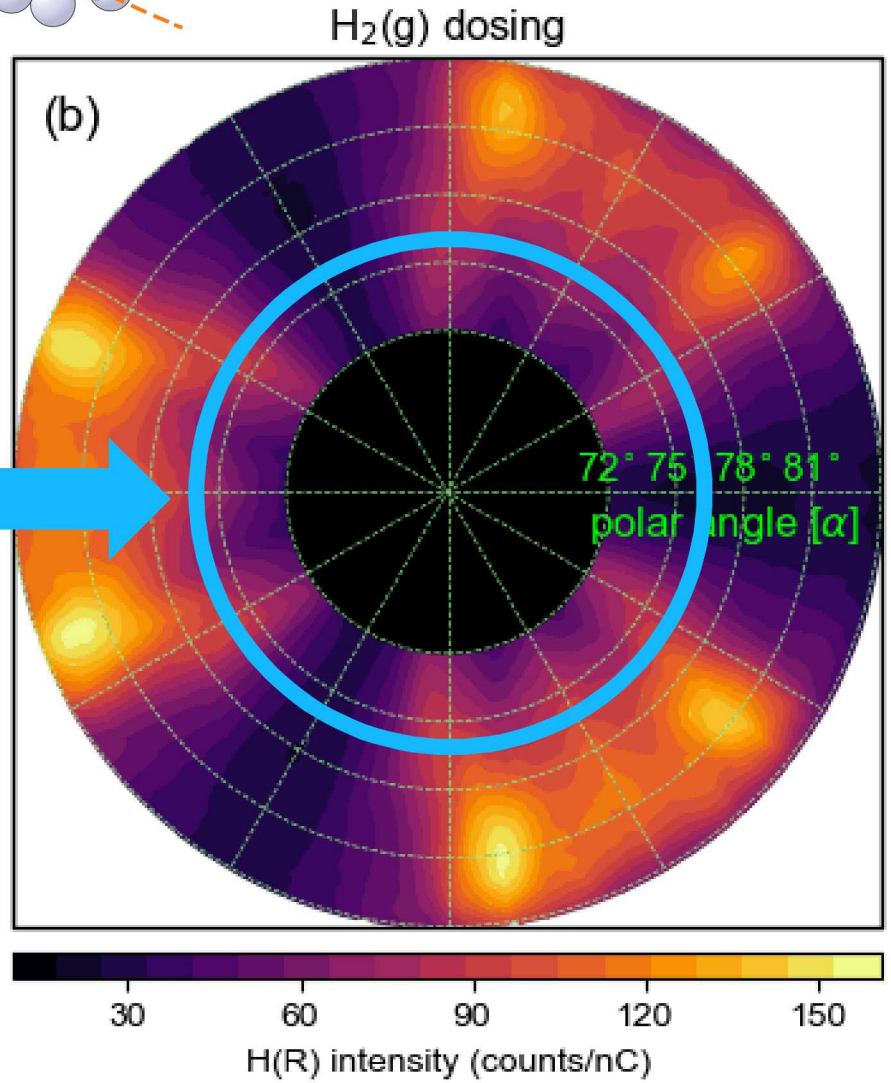


Channeling physics for the W(111)+H(ads) system

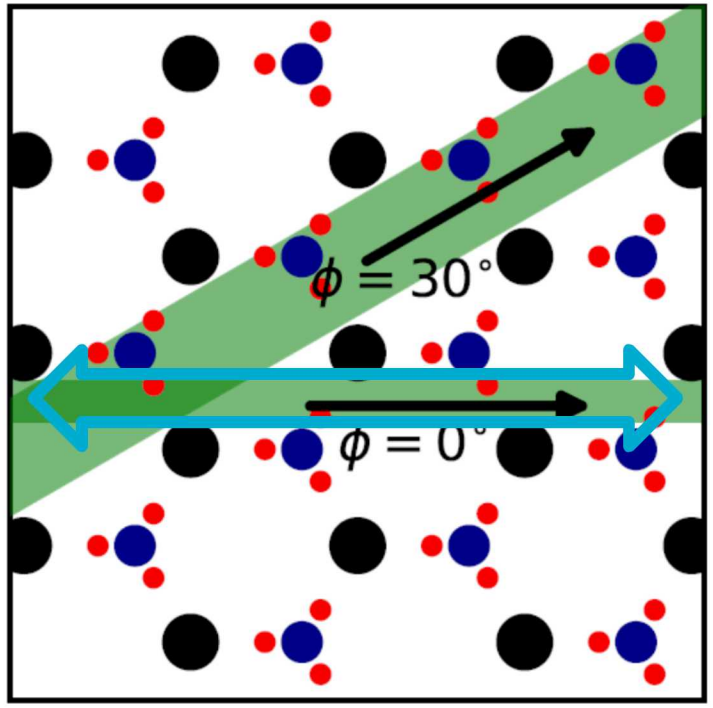
Constructing H(R) maps

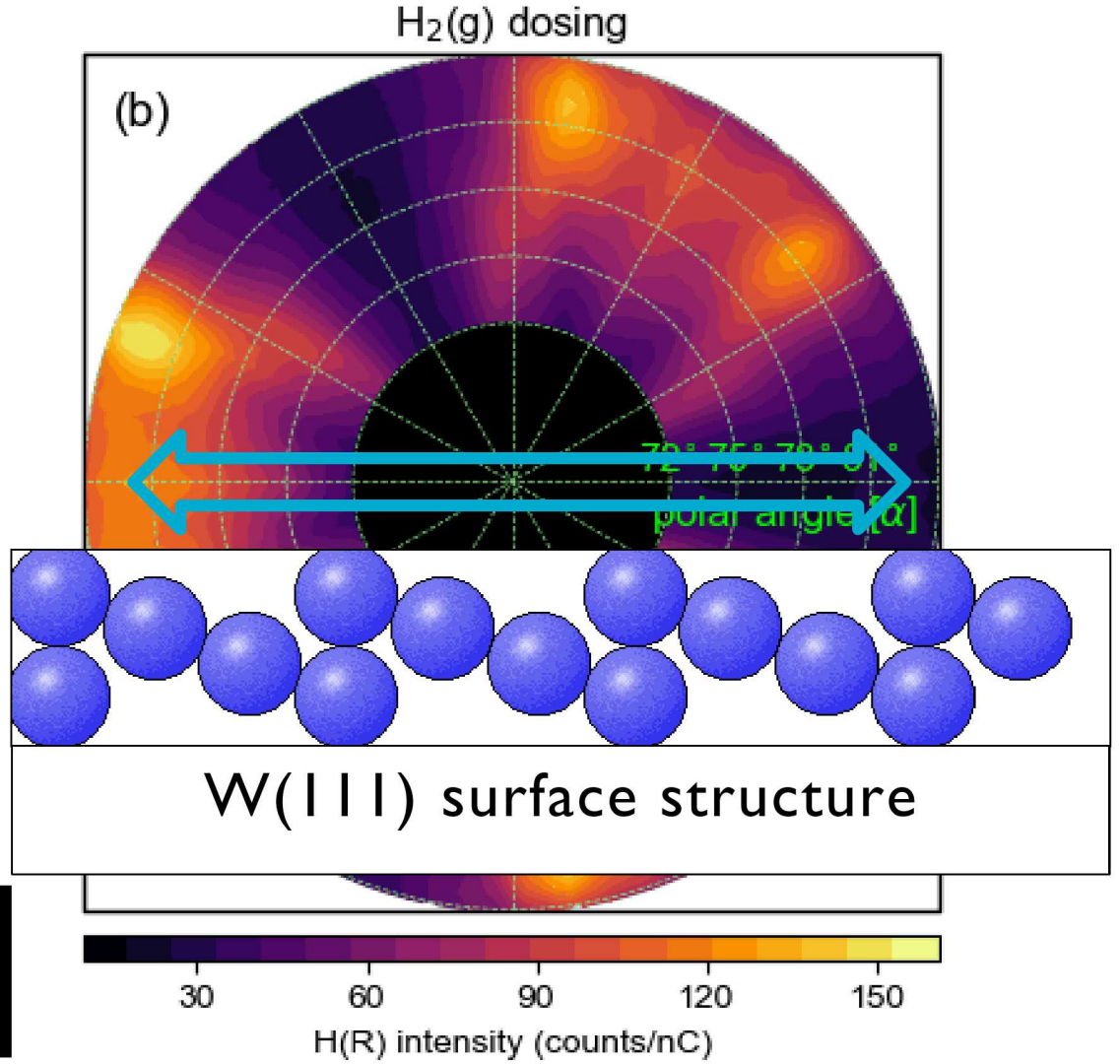






Ion channeling along and into W(111) surface

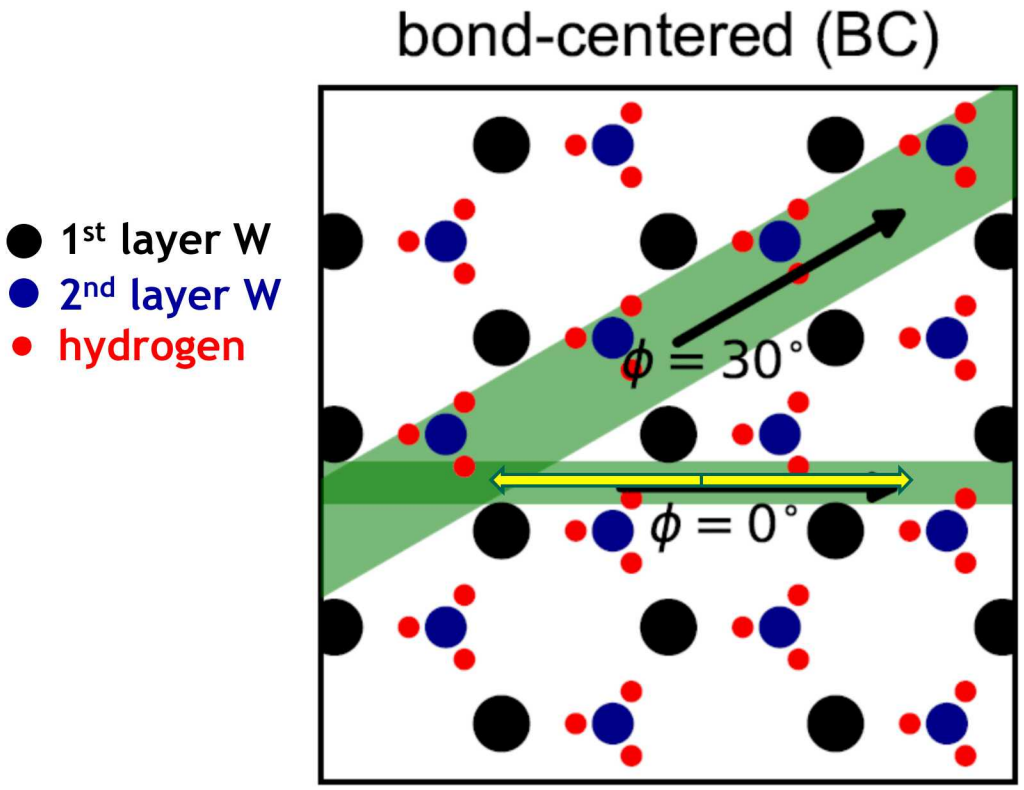


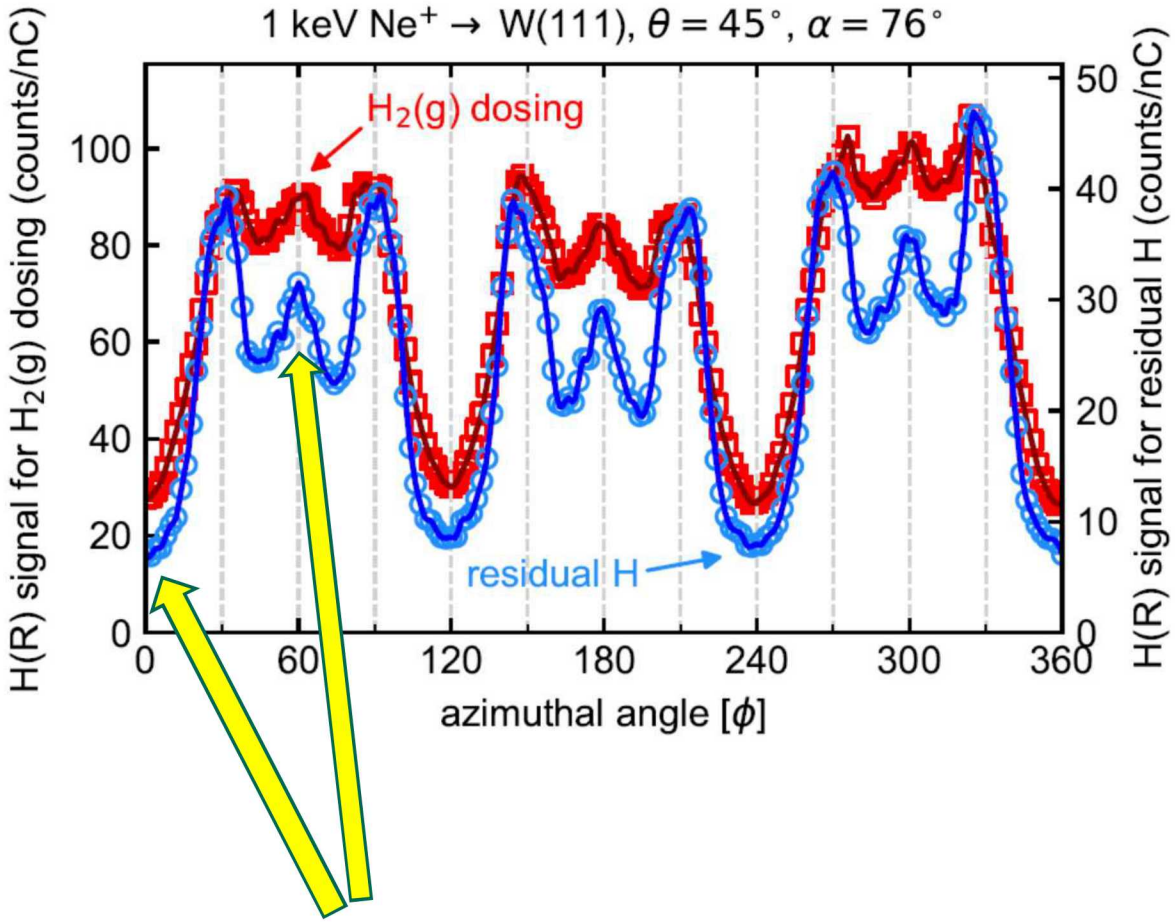


Previous studies [3]:
H within channel ➔ peak in H(R) signal

[3] Kolasinski et al., PRB, (2012).

Enhanced ion channeling due to adsorbed H





Increased signal with H dosing due to enhanced ion channeling

Summary of W(111)+H(ads) study

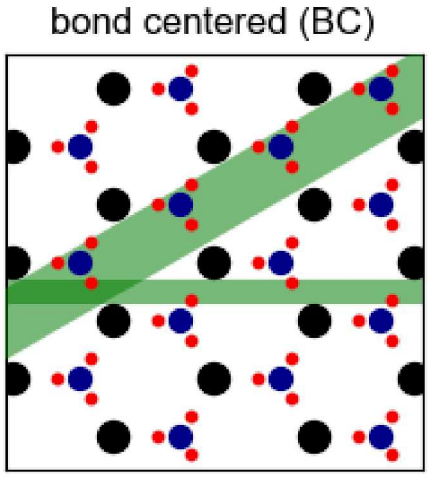
1. Advanced existing analysis and modeling techniques for surface hydrogen detection:

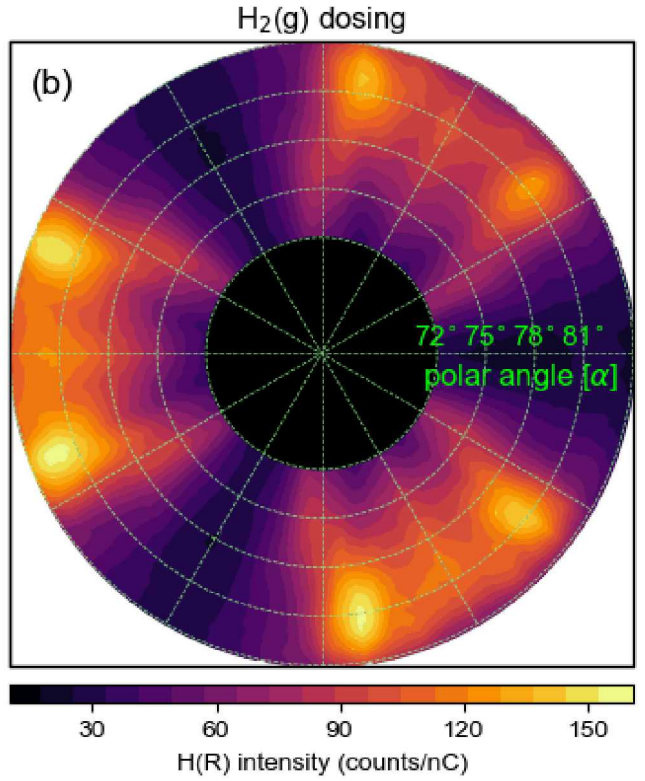
   complex binding geometry and corrugated surface

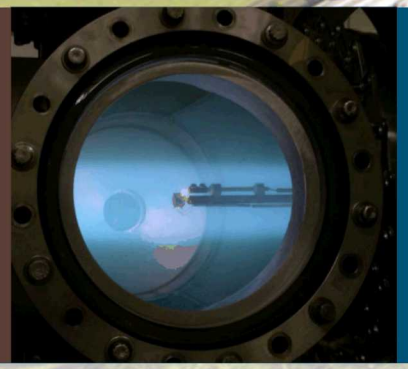
2. Validated DFT predictions:

   DFT provides inputs for larger scale models, e.g.

   - interparticle potentials for MD
   - hydrogen dissociation energies on surfaces



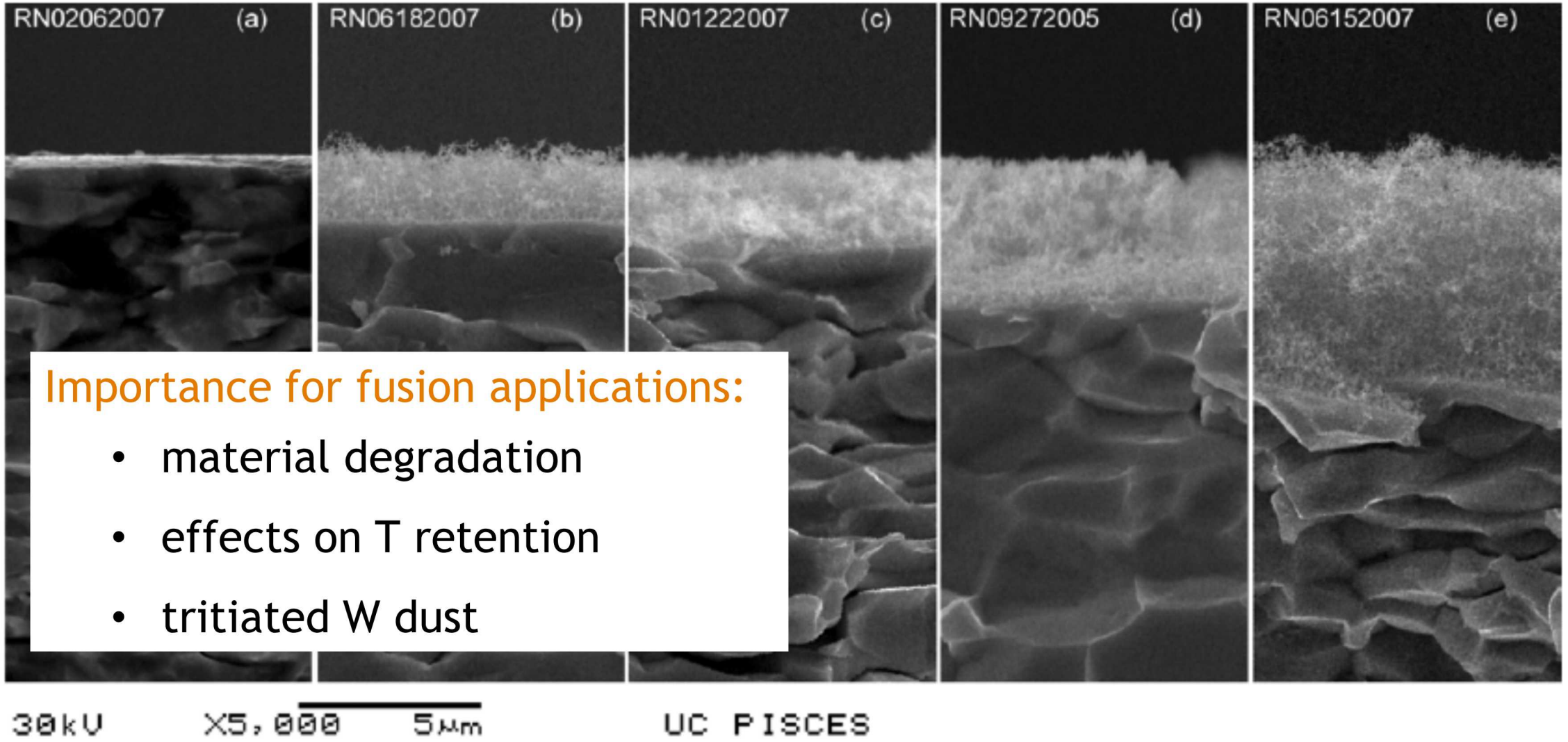




He-plasma interactions with W surfaces

Effect of TDS on He-induced W nanostructure

Helium-induced "fuzz" on W surfaces

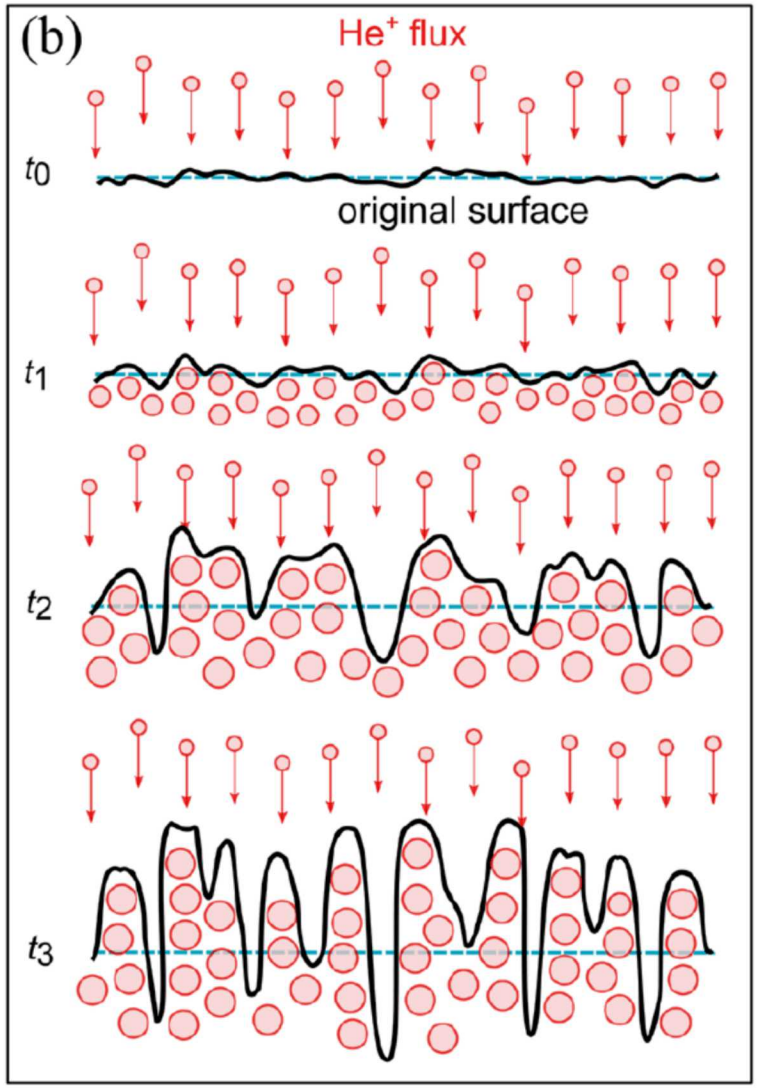


Importance for fusion applications:

- material degradation
- effects on T retention
- tritiated W dust

[6] M.J. Baldwin and R.P. Doerner, Nucl. Fusion (2008).

He-induced nanostructure growth on W surfaces



Dasgupta et al., Nucl. Fusion (2019).

- physics for fuzz growth still not well understood
- general steps:
  1. He implanted into W
  2. forms stable pairs of He
  3. coalesce into He bubbles
  4. He bubbles + surface stresses + W adatom diffusion ➔ nanostructure

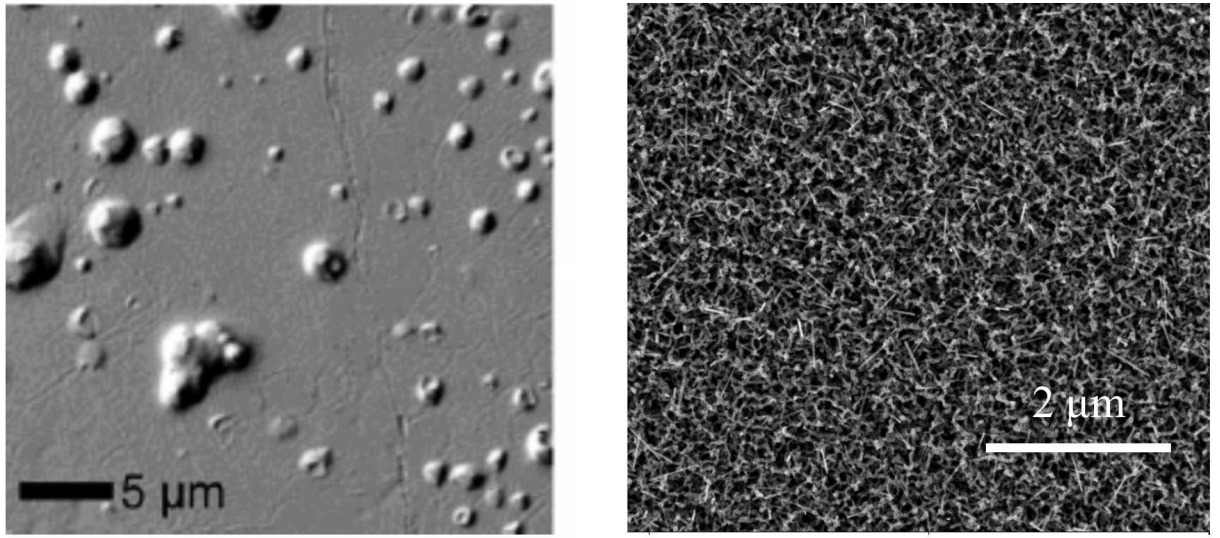
thermal desorption spectroscopy (TDS) has been applied to study He-W interactions

Thermal desorption spectroscopy (TDS)

TDS has been used to successfully study trapping energies in W

e.g. D trapping

D-exposed W vs He-exposed W



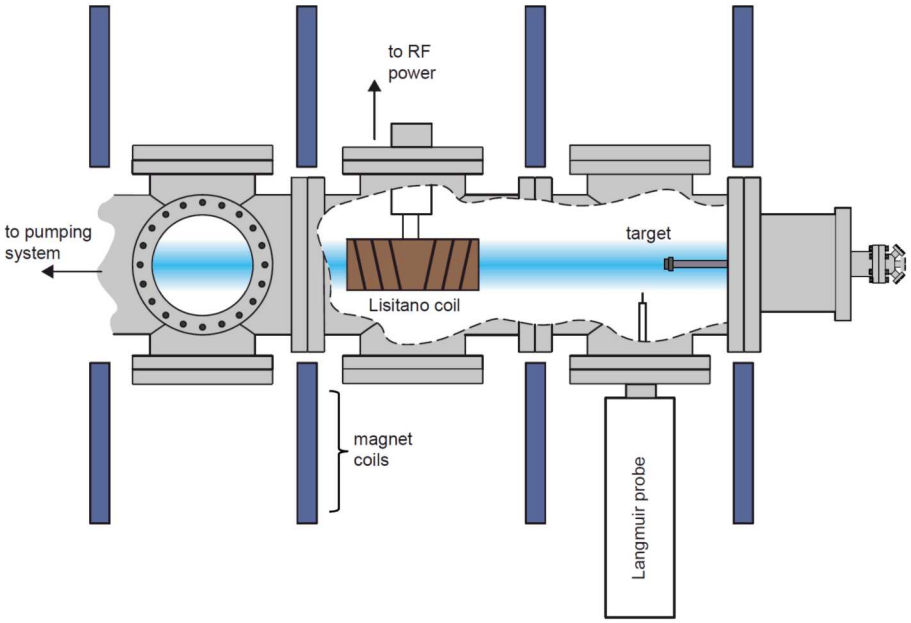
Kolasinski et al., J App. Phys., (2015).

Complications for He:

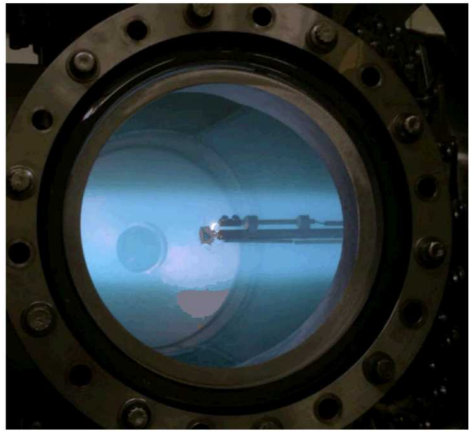
1. presence of W nanostructure
2. high *T* (>1800 K) required to fully desorb He

To what extent does the surface nanostructure change due to the high temperatures of TDS, potentially complicating TDS spectra?

Plasma exposure and conditions



DPE: Deuterium Plasma Experiment
(but with helium)



Plasma conditions

ion flux	Γ_{ion}	= 4.0 × 10^{16} cm^{-2} s^{-1}
electron temp.	T_e	= 11 eV
plasma potential	V_p	= 40 V
plasma density	n_p	= 2.0 × 10^{10} cm^{-3}

Plasma exposure (same for all samples):

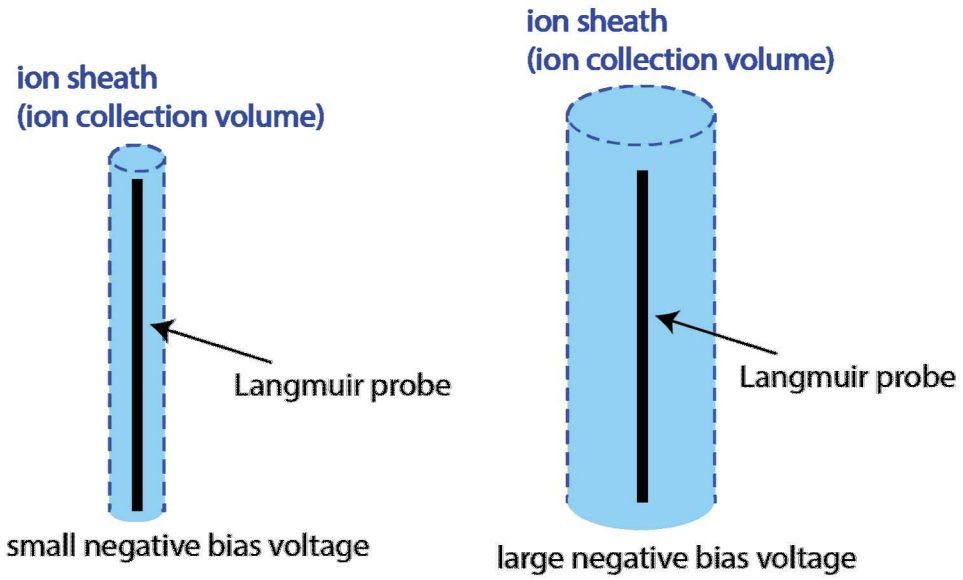
(1) 6 hours in plasma

(2) held at 850 °C

(3) biased at -50 V (ion energy of 90 eV)

Improving Langmuir Probe modeling

Added sheath expansion effect to our model

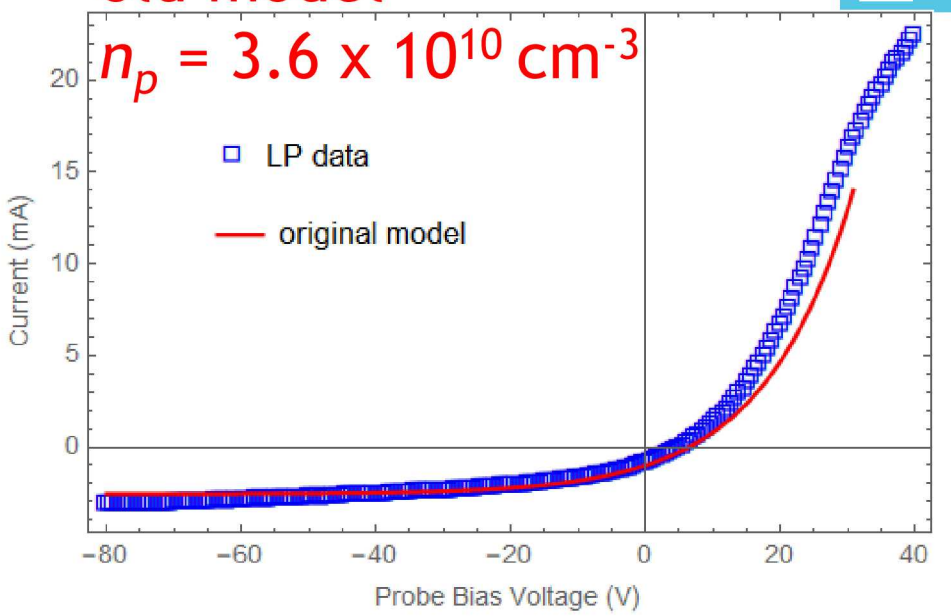


$$I = \text{ion current} + \text{electron current}$$

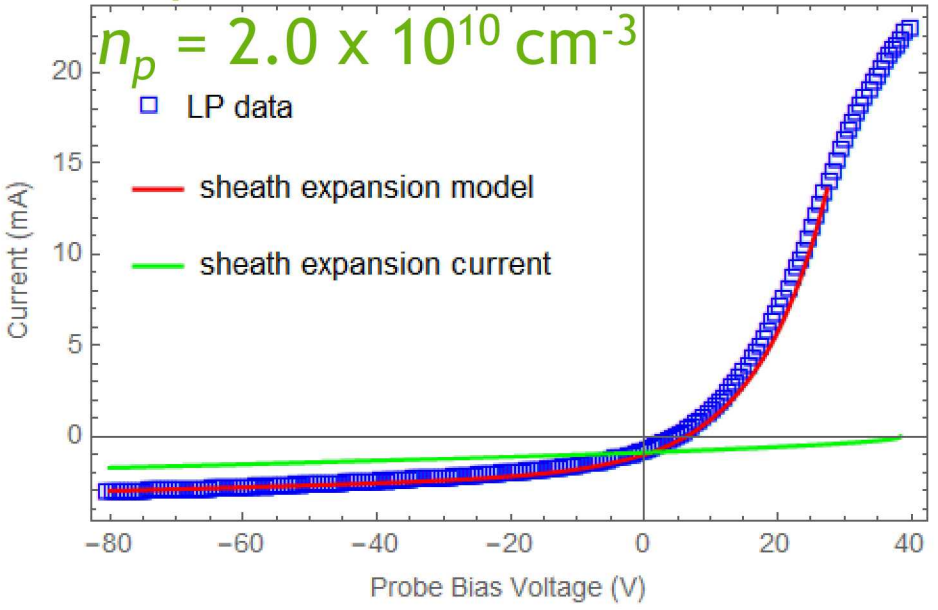
$$I = an_p\sqrt{T_e}\left(1+\frac{x_s}{a_p}\right) + bn_p\sqrt{T_e}\exp\left[\frac{e(U-V_p)}{T_e}\right]$$

does not have any additional free parameters!

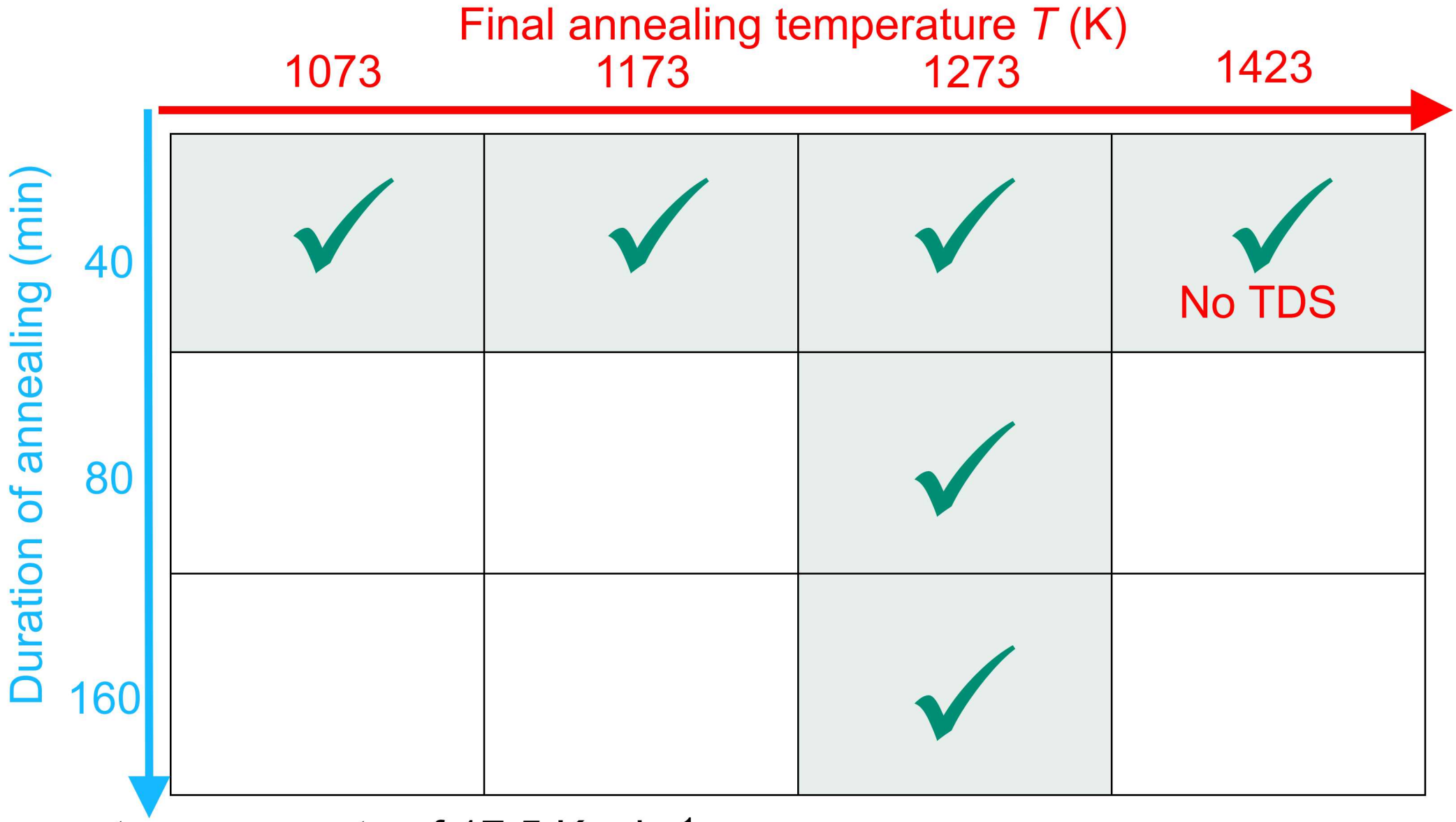
old model



improved model

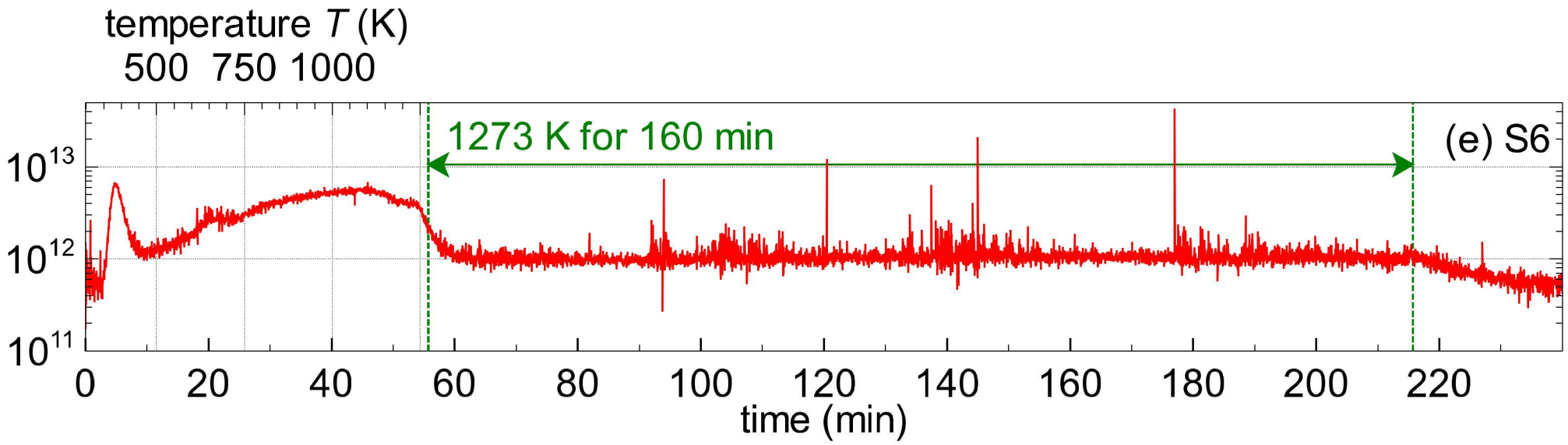


Samples annealed at various temperatures and durations



Temperature ramp rate of 17.5 K min^{-1}

Representative TDS spectrum during annealing



- consistent desorption peaks near T=373 K and 1123 K for all samples
- 1123 K peak observed in literature for similar He-plasma exposures
- spikes are indication of bursting of near-surface He bubbles

Surface characterization: HIM and SE

Helium ion microscopy

pros:

- FIB profiling to measure thickness
- better depth of field, resolution, and contrast than SEM

cons:

- performed at UC Berkeley (slow)
- ex-situ and post-mortem

zeiss.com

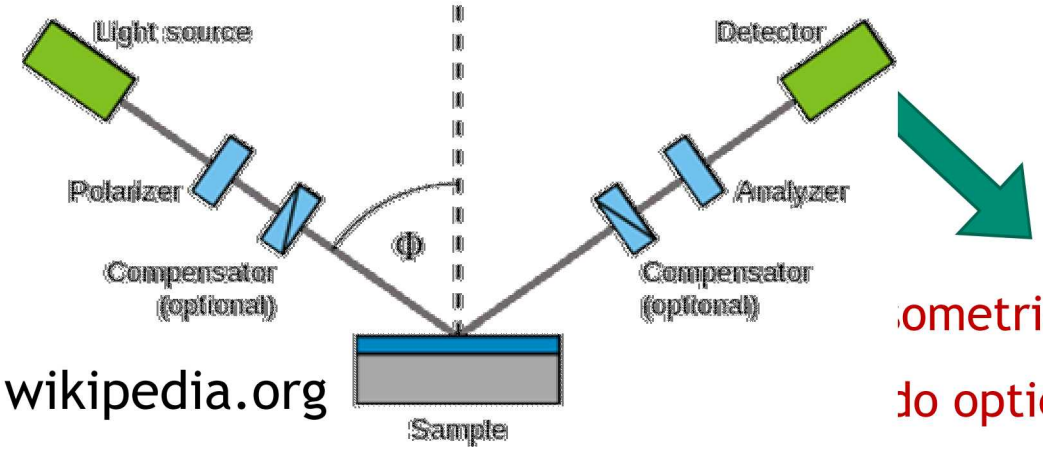
Spectroscopic ellipsometry

pros:

- can be performed in-situ and in real time
- non-destructive & contactless
- detection of nm-sized changes
- a lot of information embedded into Ψ, Δ

con:

- need to interpret data with a model or benchmark

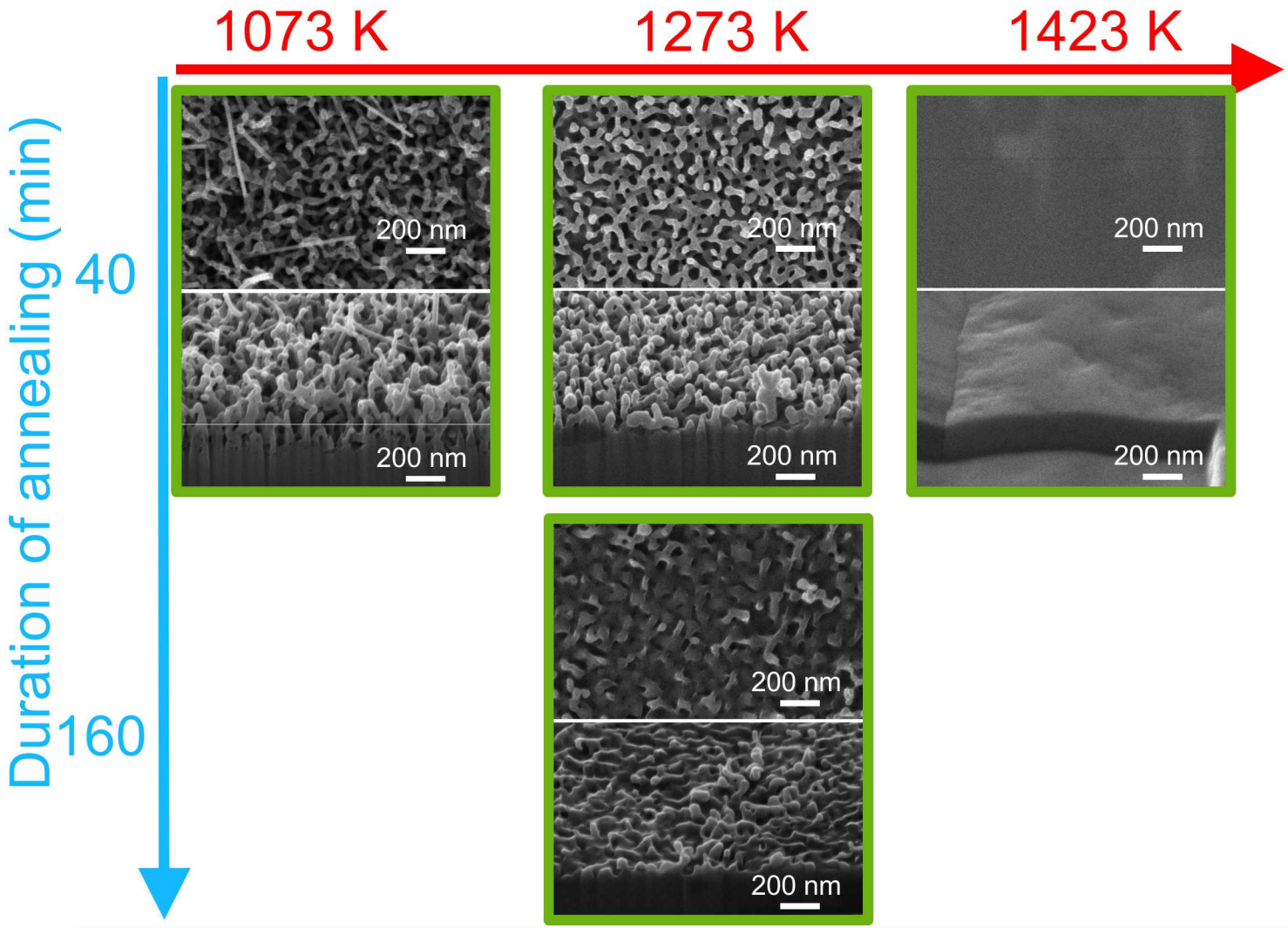


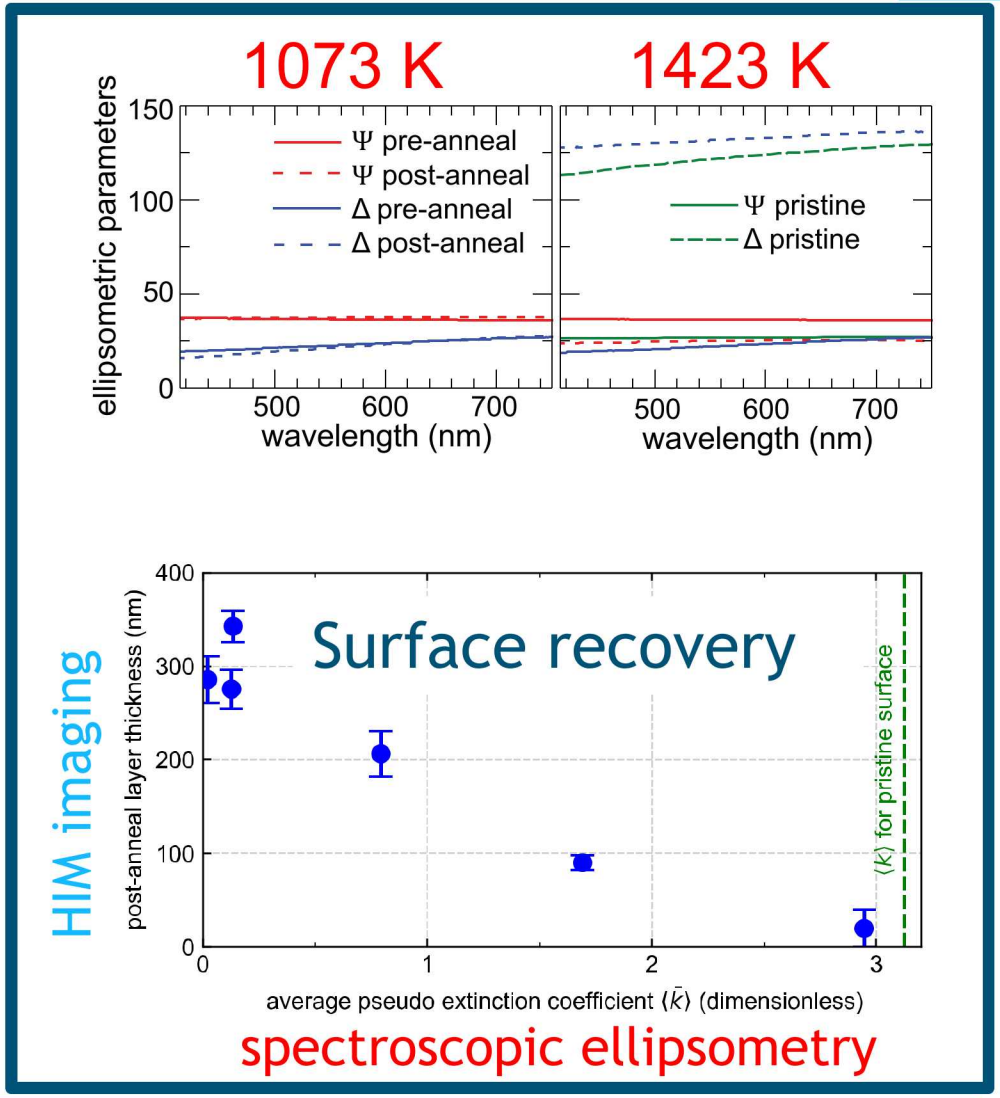
wikipedia.org

ometric parameters: Ψ, Δ

do optical constants: $\langle n \rangle$, $\langle k \rangle$

Surface characterization after annealing



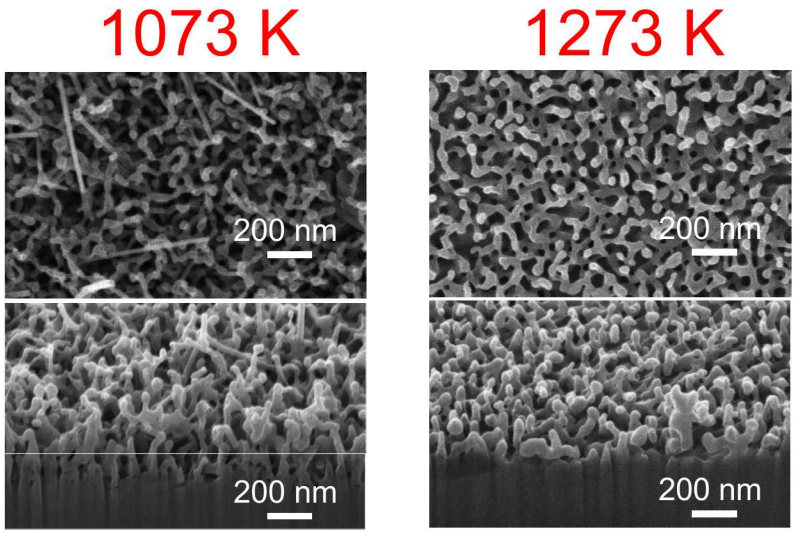


1) changes to surface morphology occur at relatively low temperatures (<1800 K)

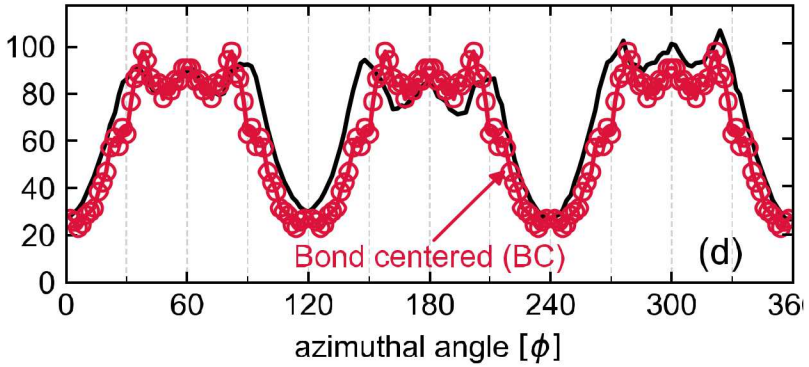
2) potential use of ellipsometry to track surface recovery in-situ

Summary

1. Validated bond centered (BC) hydrogen binding for the W(111)+H(ads) system



2. TDS of He-induced W nanostructure
   - changes in morphology observed at 1273 K (>1800 K needed to fully desorb He)
   - interpretation of TDS spectra should account for changes in surface nanostructure



Thank you for your attention!

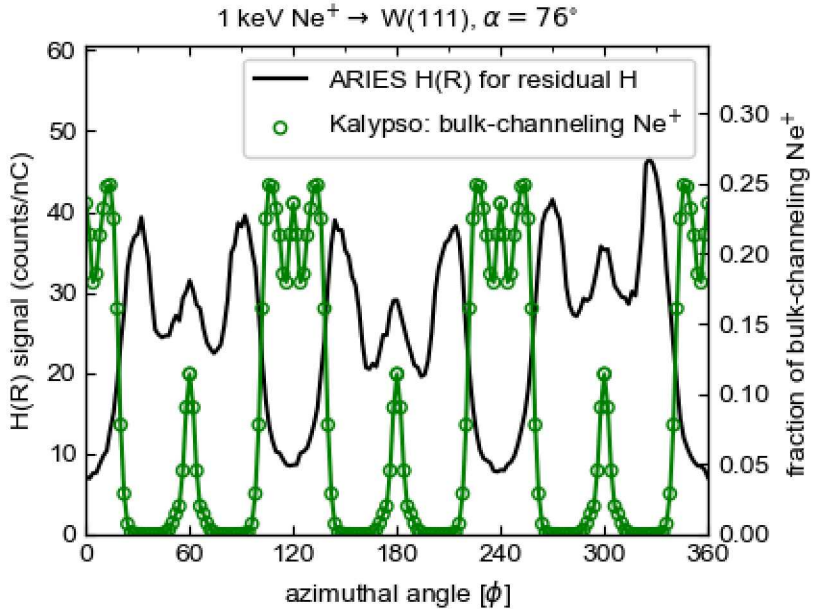
Extra slides

Ion-sheath expansion term (Child-Langmuir law)

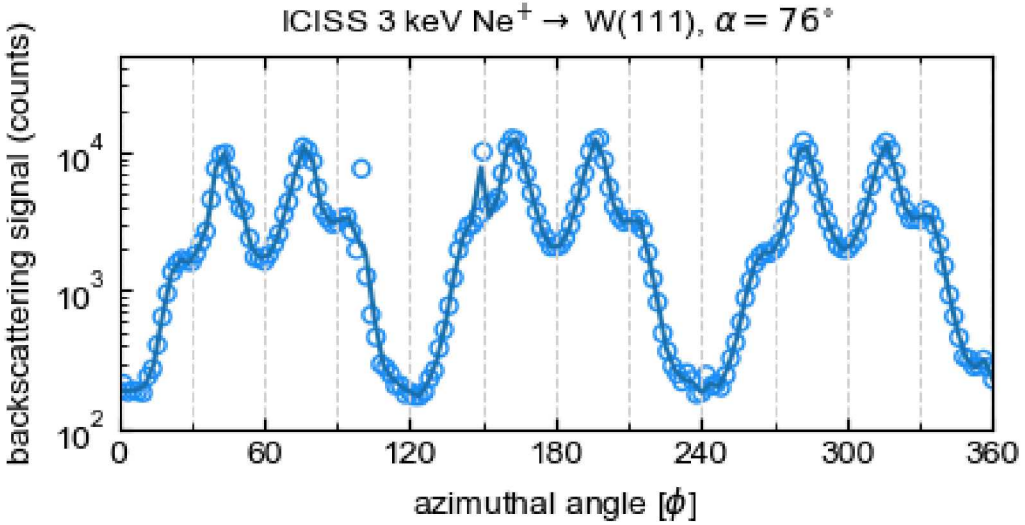
$$x_s = 1.02\lambda_D \left[\sqrt{\frac{e(U-V_p)}{T_e}} - \frac{1}{\sqrt{2}}\right]^{1/2} \left[\sqrt{\frac{e(U-V_p)}{T_e}} + \sqrt{2}\right]^{1/2}$$

Channeling into the surface breaks symmetry

MD simulation data



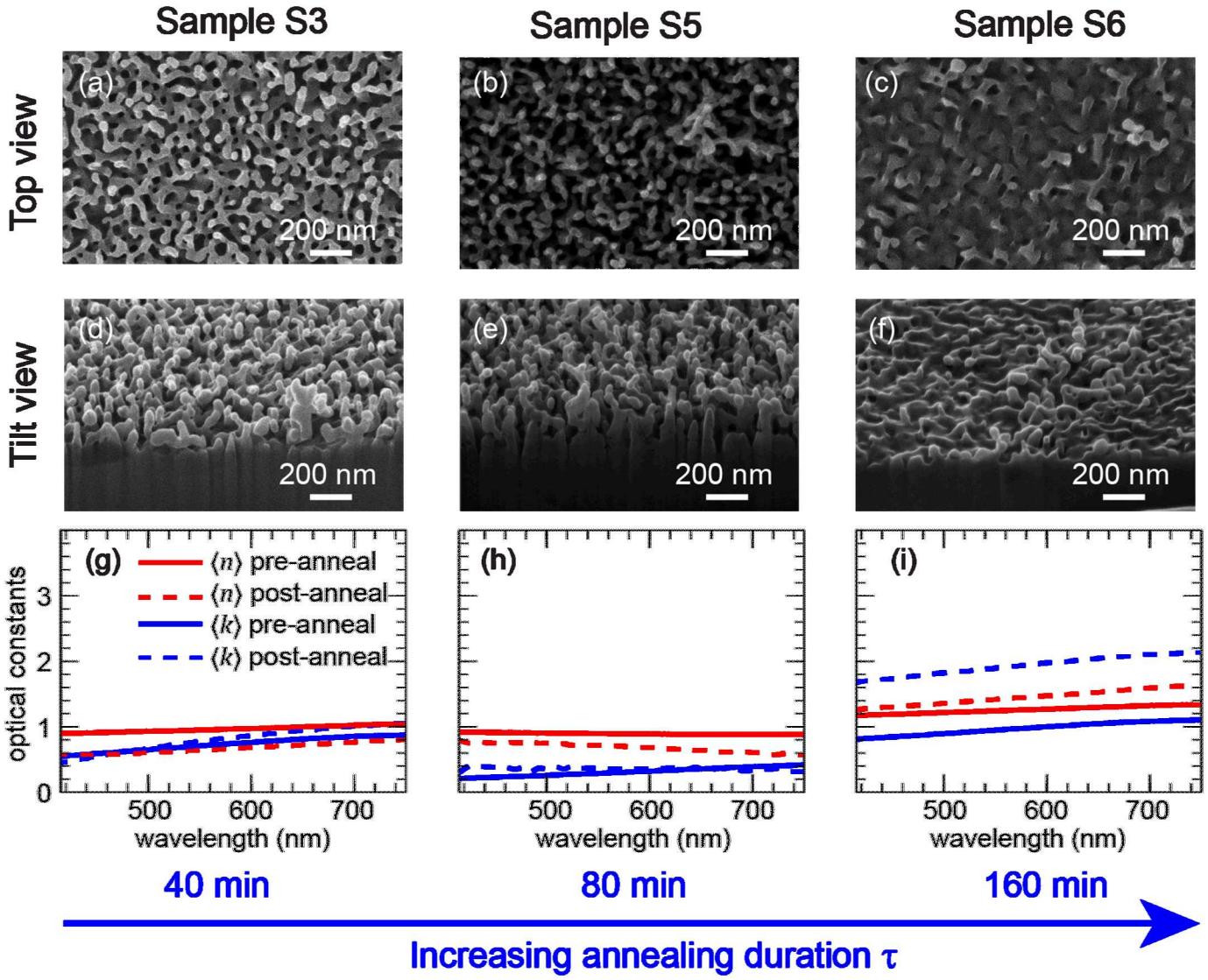
Experimental data



Channeling into surface correlate to H(R) minima

ICISS minima = maximum channeling into surface

Effect of duration on surface morphology



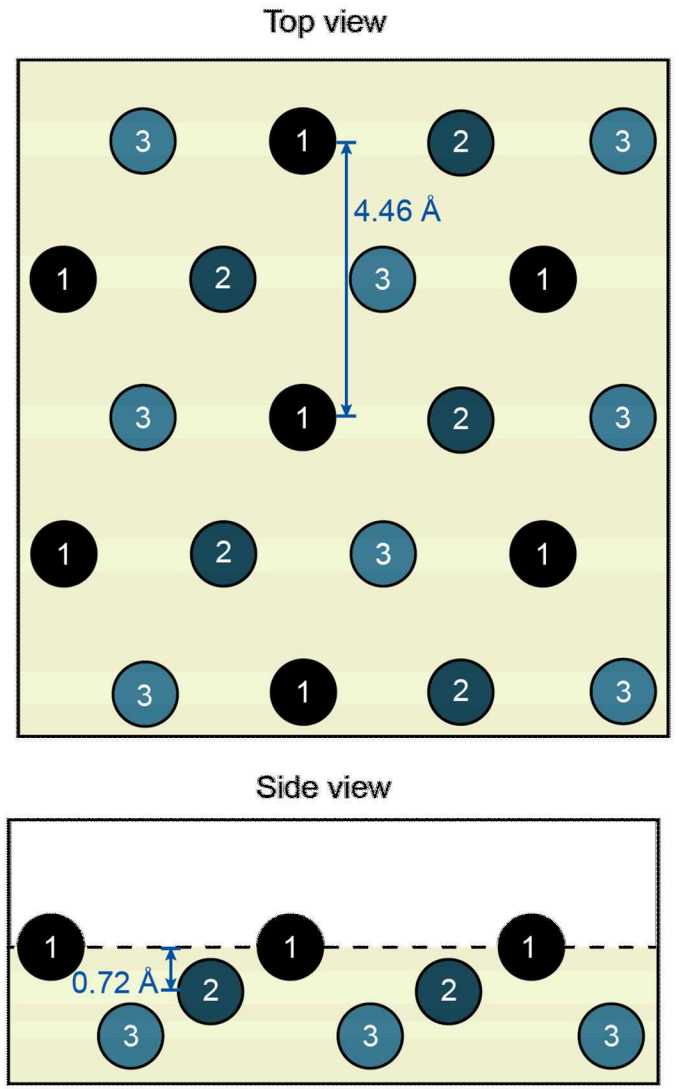
held at T = 1273 K

Nearly complete reintegration of nanostructure after 160 min

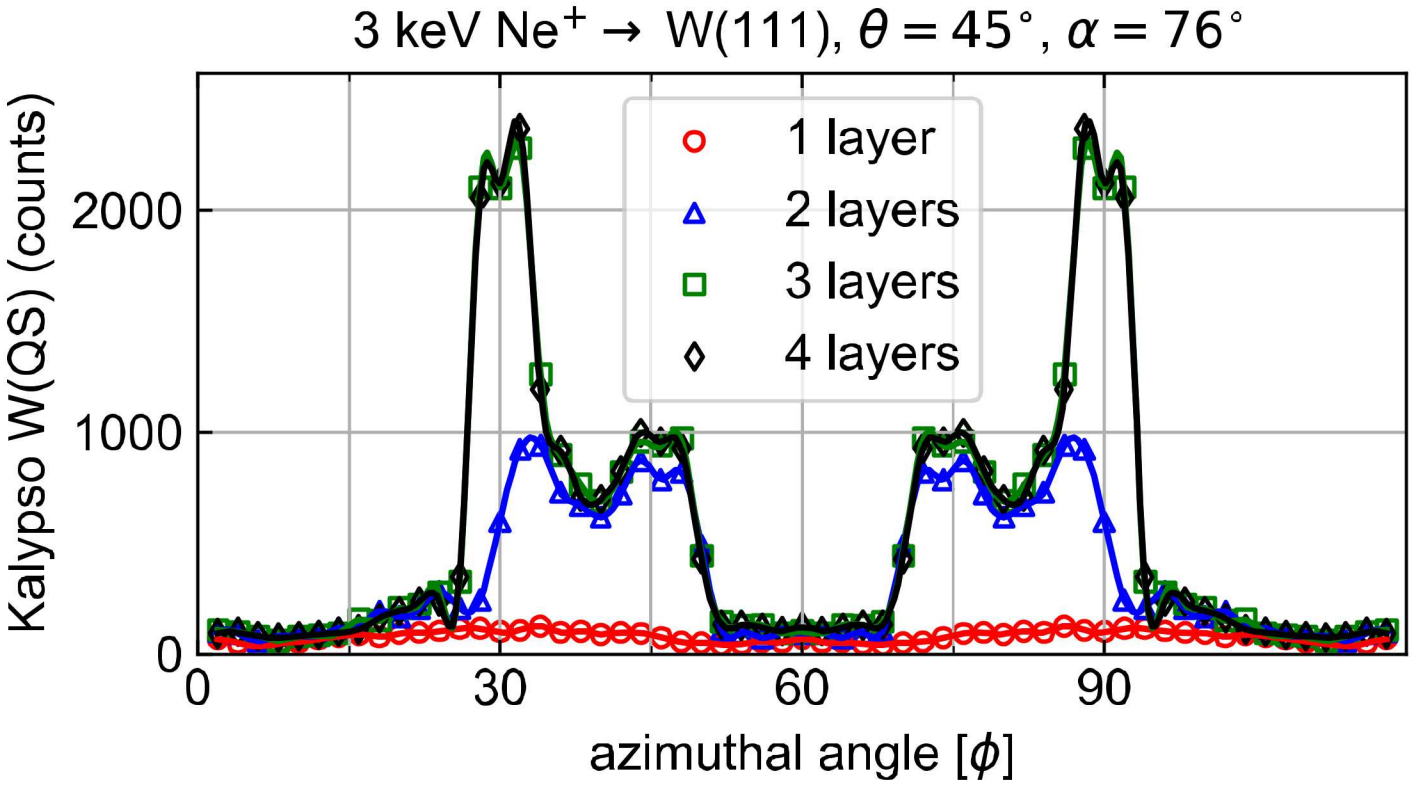
Multi-layer scattering effects for W(111)

W(111) has a very open surface structure

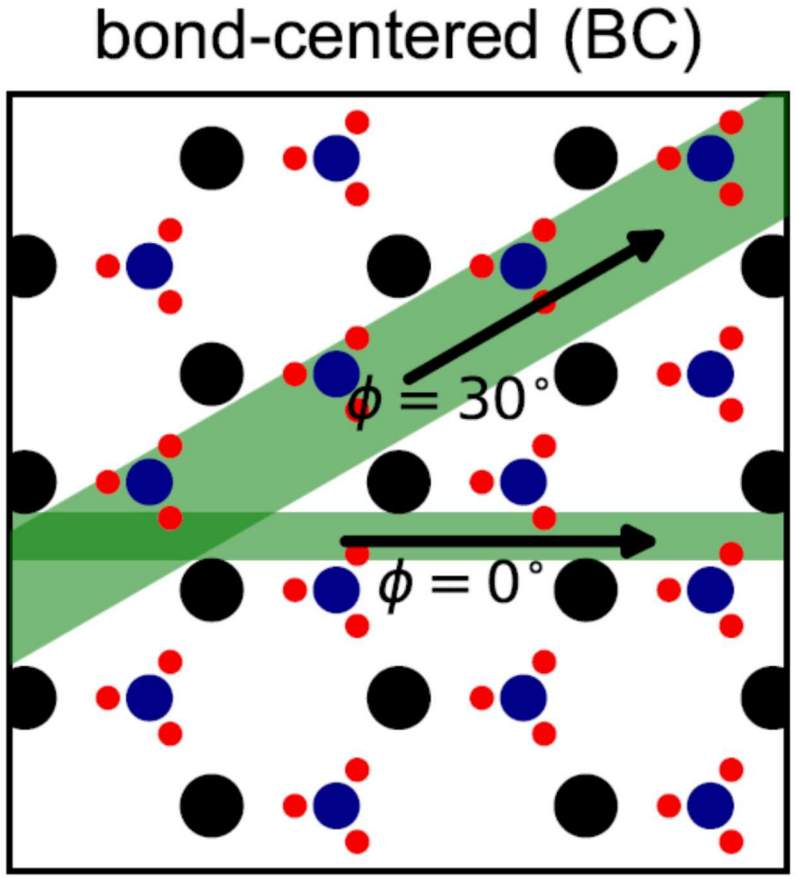
- surface atoms are far apart
- short inter-planar distances
- multi-layer scattering processes become important

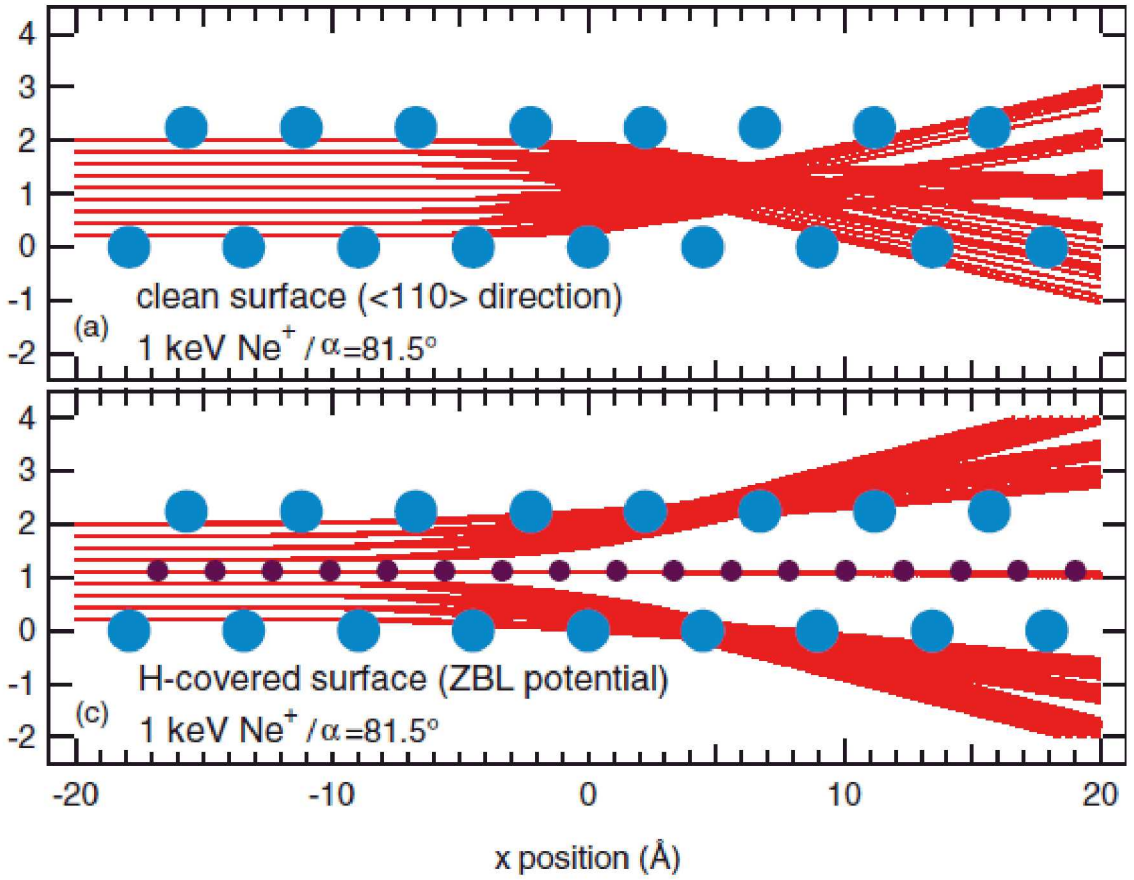


MD simulation for multi-layer scattering



Effect of hydrogen on ion-channeling

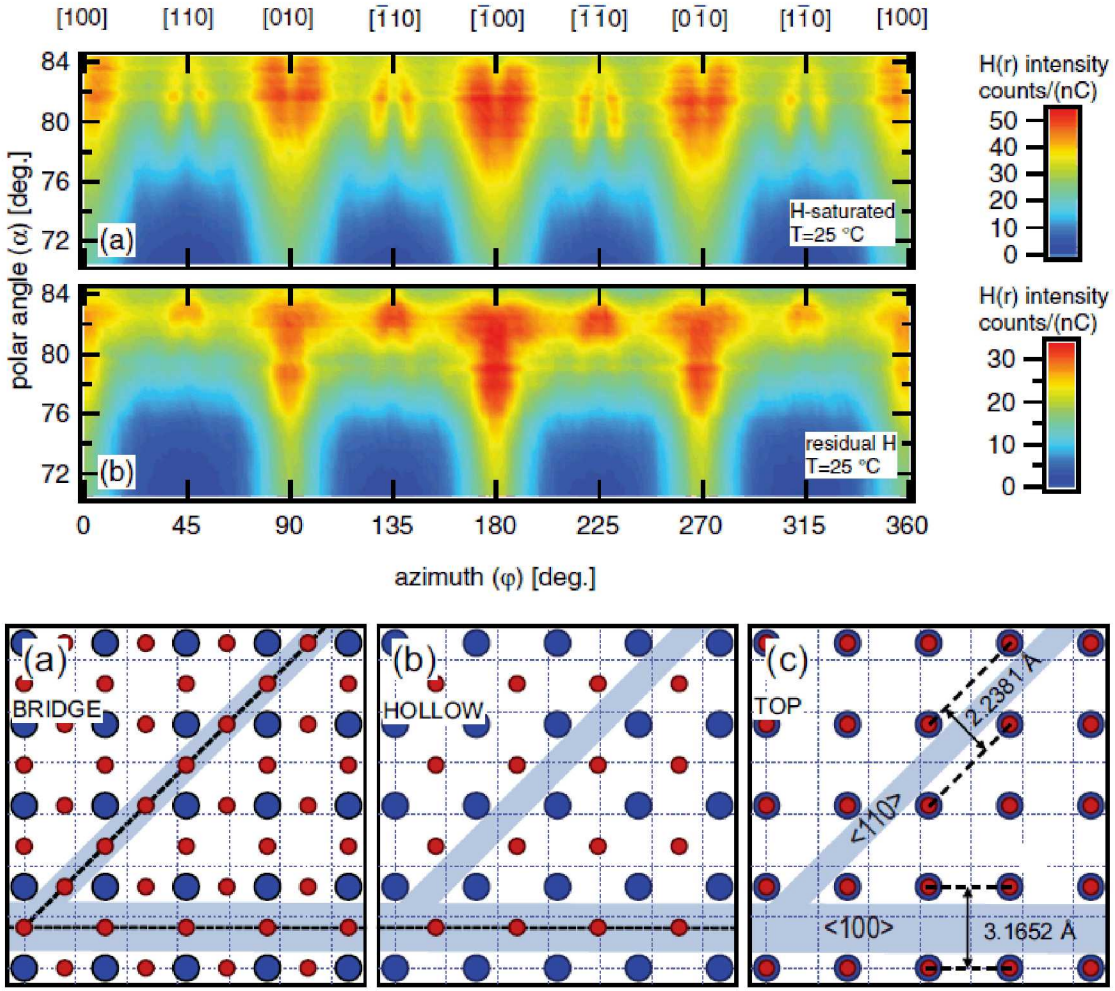


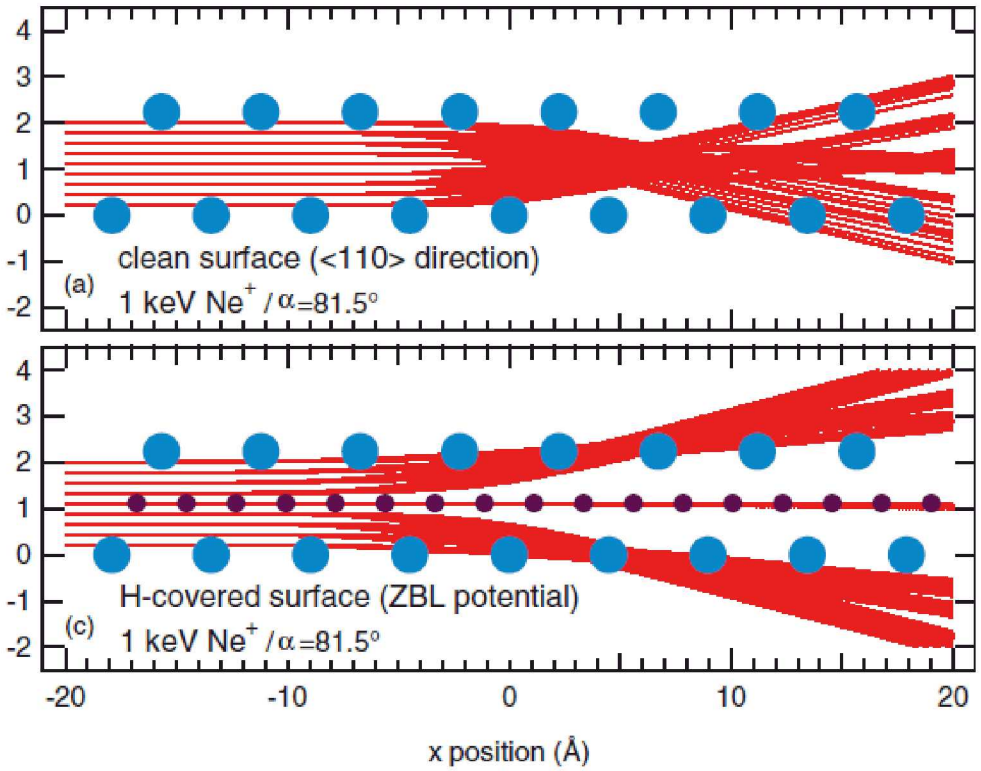


[1] Kolasinski et al., PRB 2012.

State of the art: dechanneling of projectile ions

Surface channeling in W(100)





[1] Kolasinski et al., PRB 2012.

Constraining adsorbate position

We find d_{BC} = 1.6 ± 0.1 Å

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1.49 Å ≤ d_{BC} ≤ 1.69 Å