2025/05/26

Adsorption and in-diffusion of Hydrogen at metal and metal oxide surfaces

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M. Wilde, K. Kato

Outline

1. Introduction: Interaction of Hydrogen with materials

"Surface science / thin film point of view"

2. Experimental methods

    Various hydrogen beams

    Nuclear reaction analysis: H depth profiling & site analysis

3. Results and Discussion

    ・Metal oxides

        Perovskite: $SrTiO_3$, High-entropy alloy, $ReNiO_3$

        TiO_2: rutile vs. anatase

    ・Metal: metastable hydrides of Pd and Pt

4. Summary

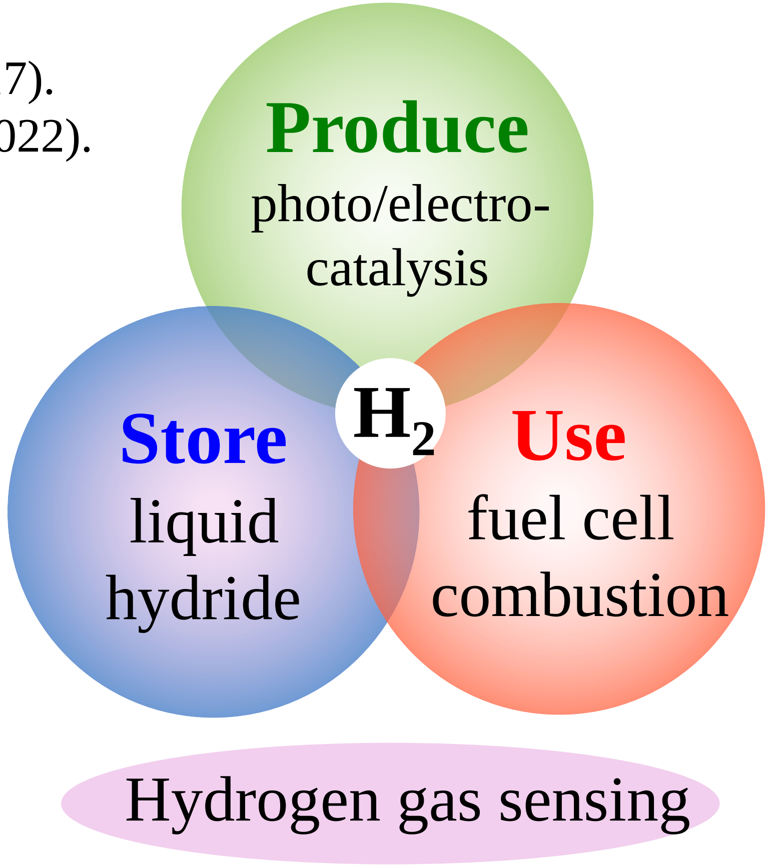
Interaction of Hydrogen with materials

- Hydrogen is a clean energy (no CO_2 emission)

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O + Q(286\ \mathrm{kJ/mol})$$

Chem. Rec. 17, 233 (2017).
Catal. Lett. 152, 1583 (2022).

- ✓ Hydrogeneration / de-hydrogenation reactions at surfaces
- ✓ Hydrogen in-diffusion & hydride formation



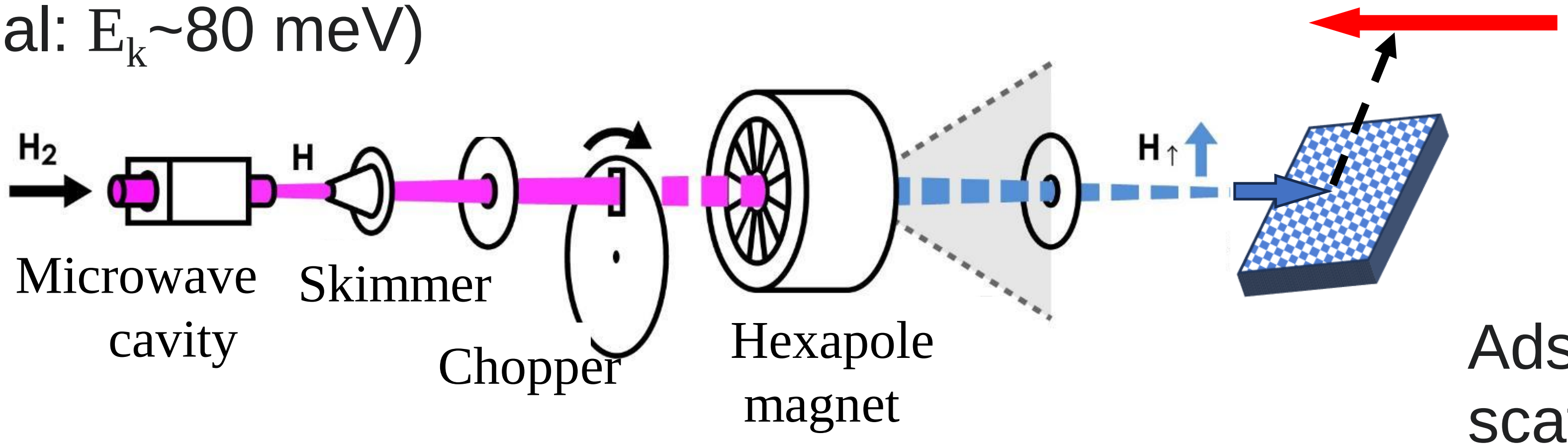
- Control of physical properties by hydrogen
  - ✓ Switchable mirrors: YHx (J.N. Huiberts et al., Nature 380, 231 (1996))
  - ✓ Superconductivity: LaH_x (Tc~240 K) E. Snider et al., Nature 586, 373 (2020)

etc.

Hydrogen beam

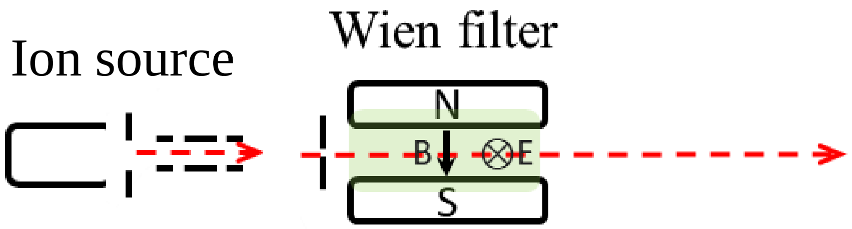
Molecular H_2 / Atomic H
(thermal: E_k~80 meV)

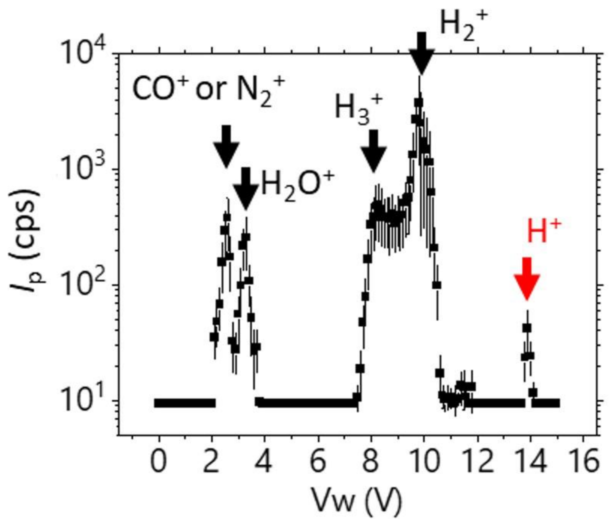
REMPI Laser



Adsorption, desorption scattering, permeation

Low-energy H_2^+, H^+
(a few eV ≤ E_k ≤ 2 keV)





Characterization by TDS / NRA

T. Terasawa et al., e-J. Surf. Sci. Nanotech. 20, 196 (2022)

H. Ueta et al., PRB 102, 121407(R) (2020); JPCL 14, 7591 (2023)

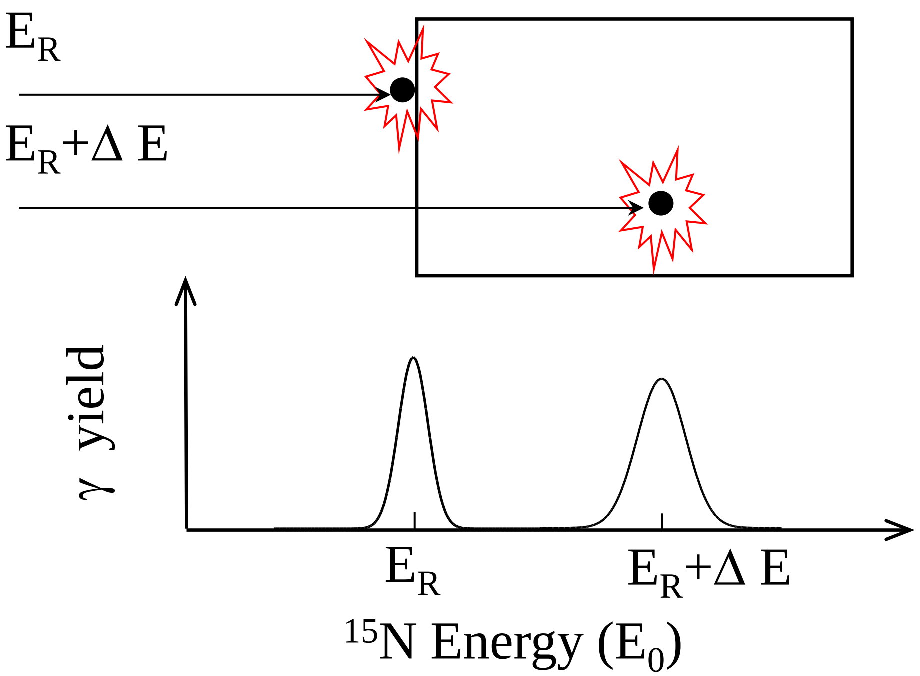
Y. Nagaya et al., JCP 155, 194201 (2021)

Nuclear Reaction Analysis

$^{15}N + ^{1}H \rightarrow ^{12}C + \alpha + \gamma$ (4.43MeV)

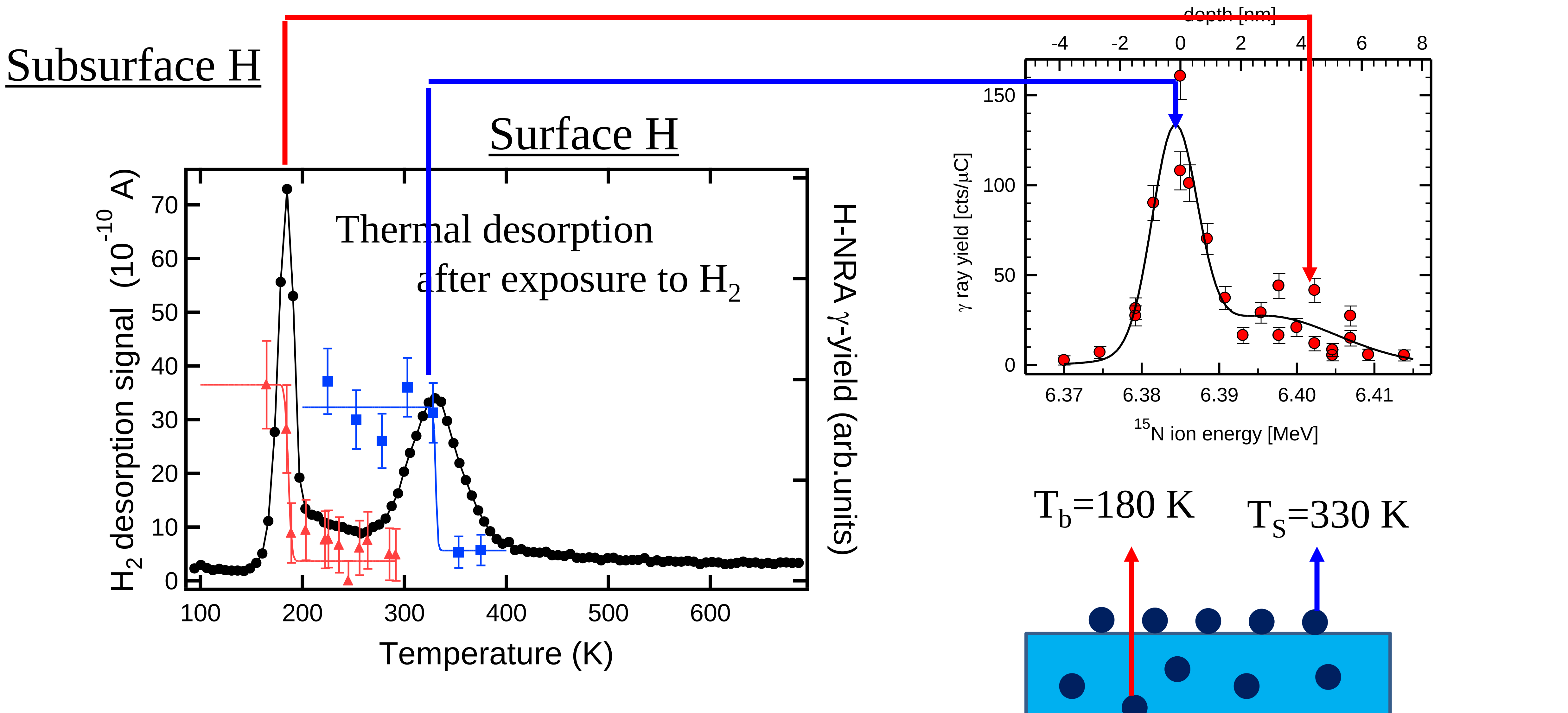
Resonance at E_R= 6.385 MeV   Resonance width= 1.8 keV

Depth profiling



M. Wilde & KF, Surf. Sci. Rep. 69 (2014) 196.

H storage in Pd



Surf. Sci. 482-485 (2001) 346; Phys. Rev. B 78 (2008) 115411.

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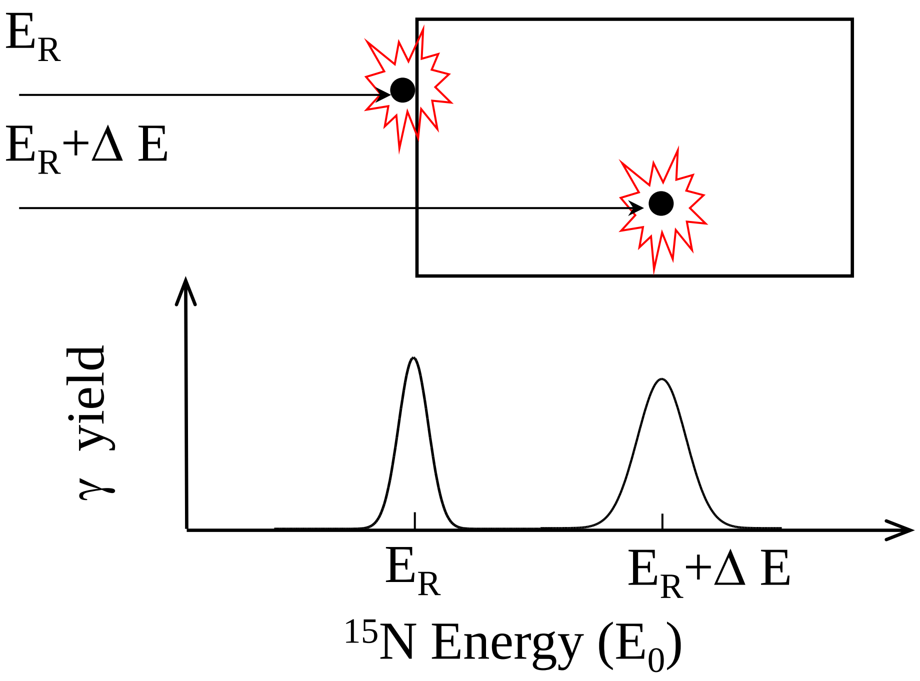
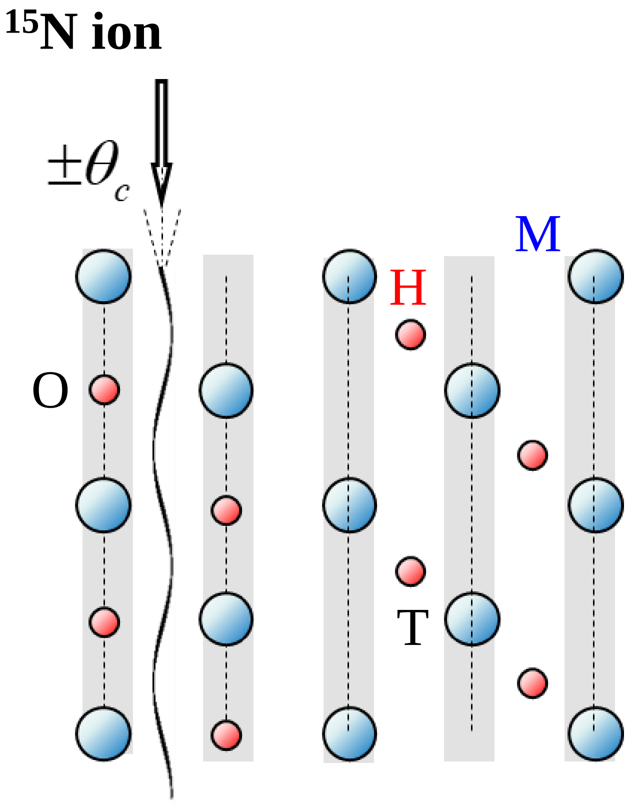
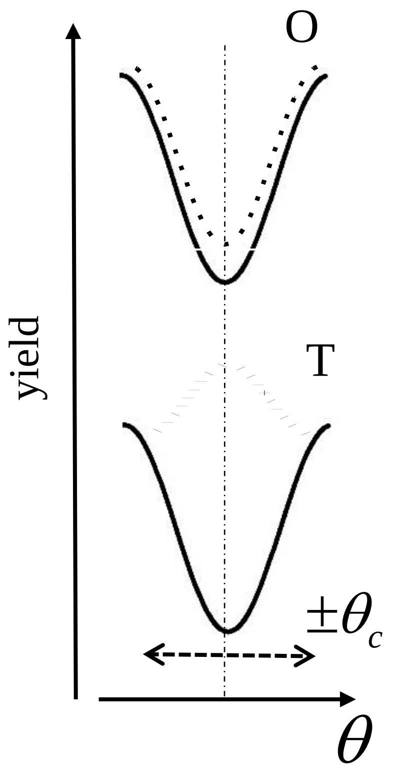


Channeling



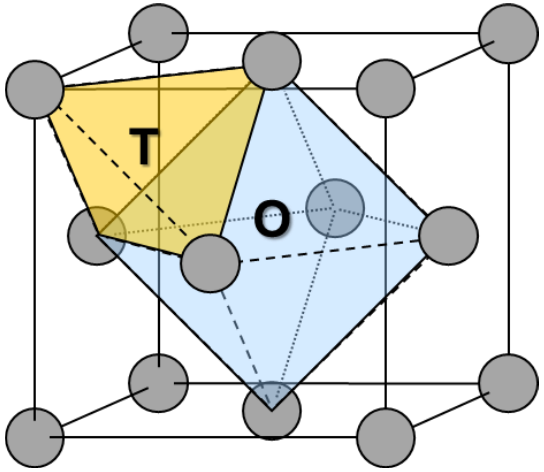
Site analysis



M. Wilde & KF, Surf. Sci. Rep. 69 (2014) 196.

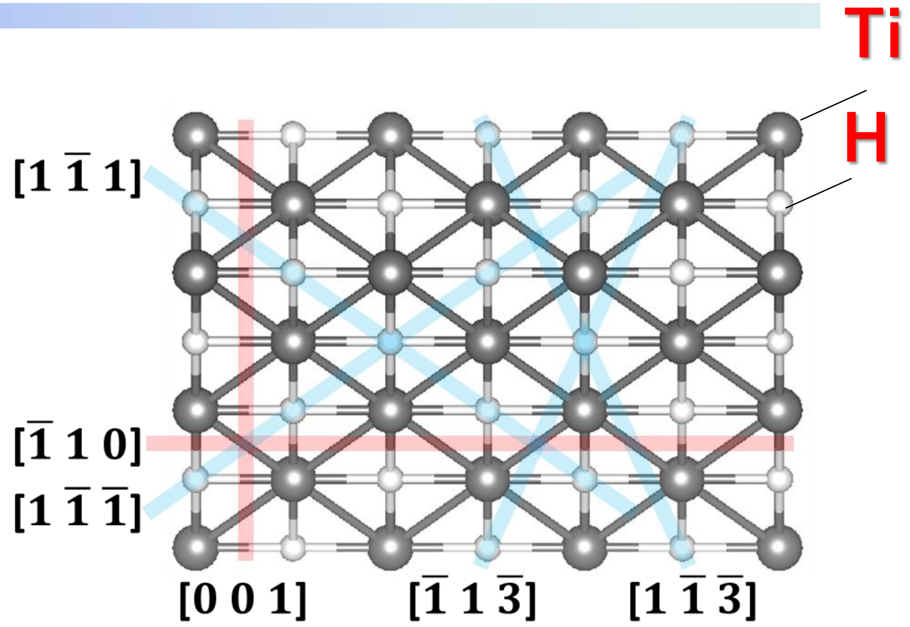
Analysis of H location: TiH_{2-x}

Fcc



Visible
Hidden

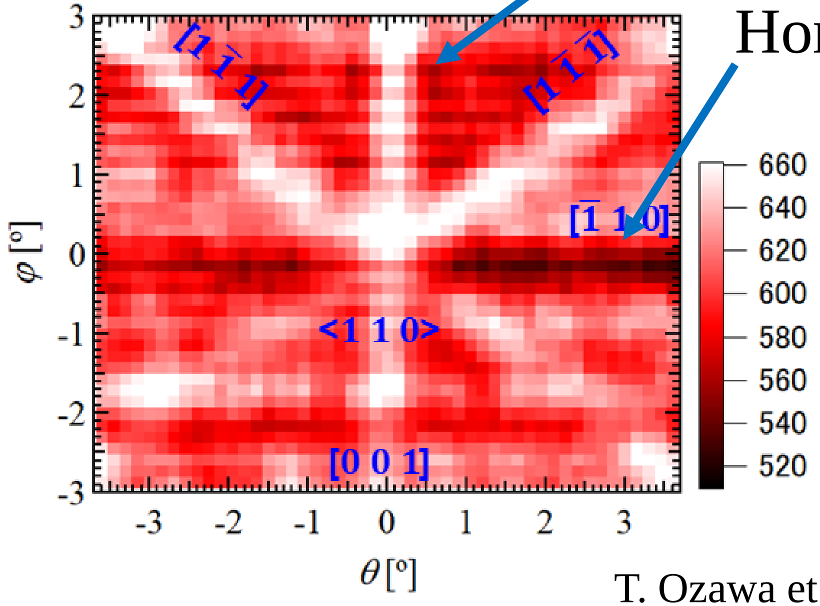
H in
O site



Vertical: bright

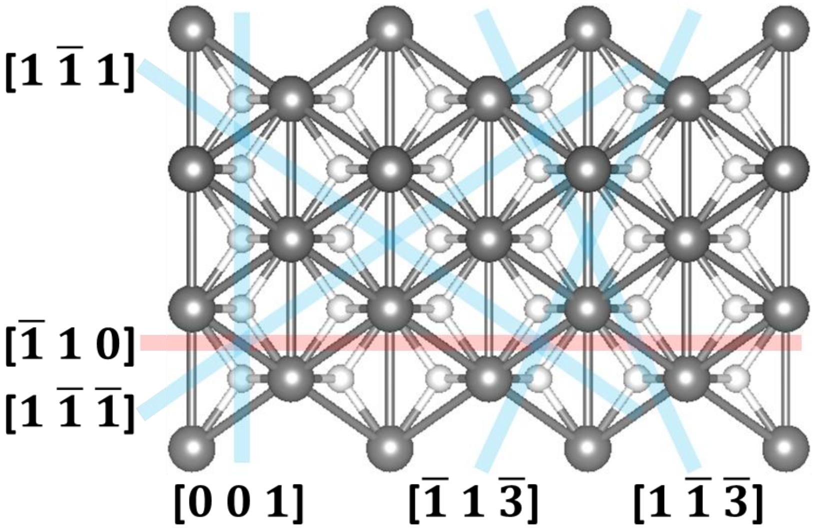
Horizontal: dark

H-NRA



H in
T site

10%H in
O site



T. Ozawa et al., Nat. Commun. 15, 9558 (2024).

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    Perovskite: $SrTiO_3$, High-entropy alloy, $ReNiO_3$

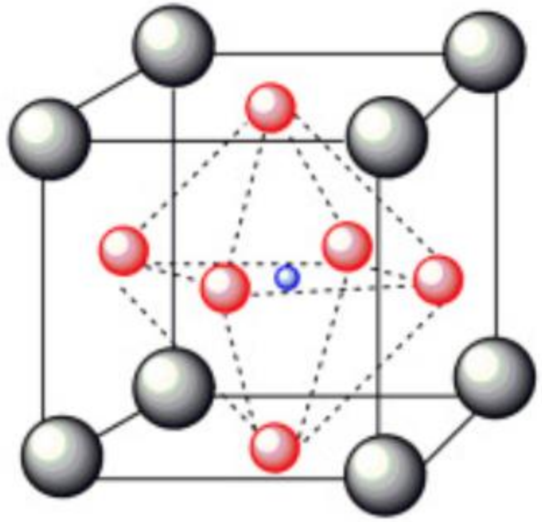
    TiO_2: rutile vs. anatase

- Metal: metastable hydrides of Pd and Pt

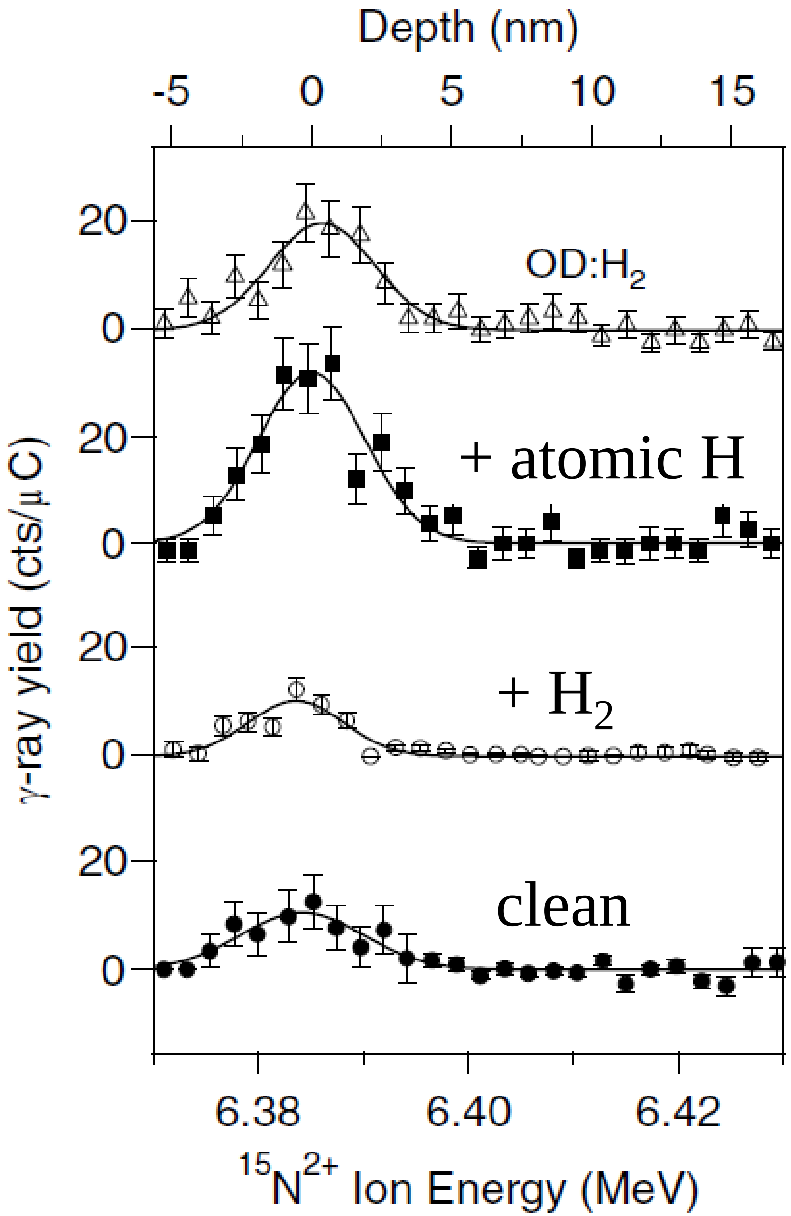
4. Summary

Perovskite metal oxide: $SrTiO_3$ (001)

$SrTiO_3$ (001)



Two types of surfaces
SrO & TiO_2 (001)



H-induced conductivity
=Dielectric breakdown

H density
3.1 ± 0.7 (10^{14} cm^{-2})

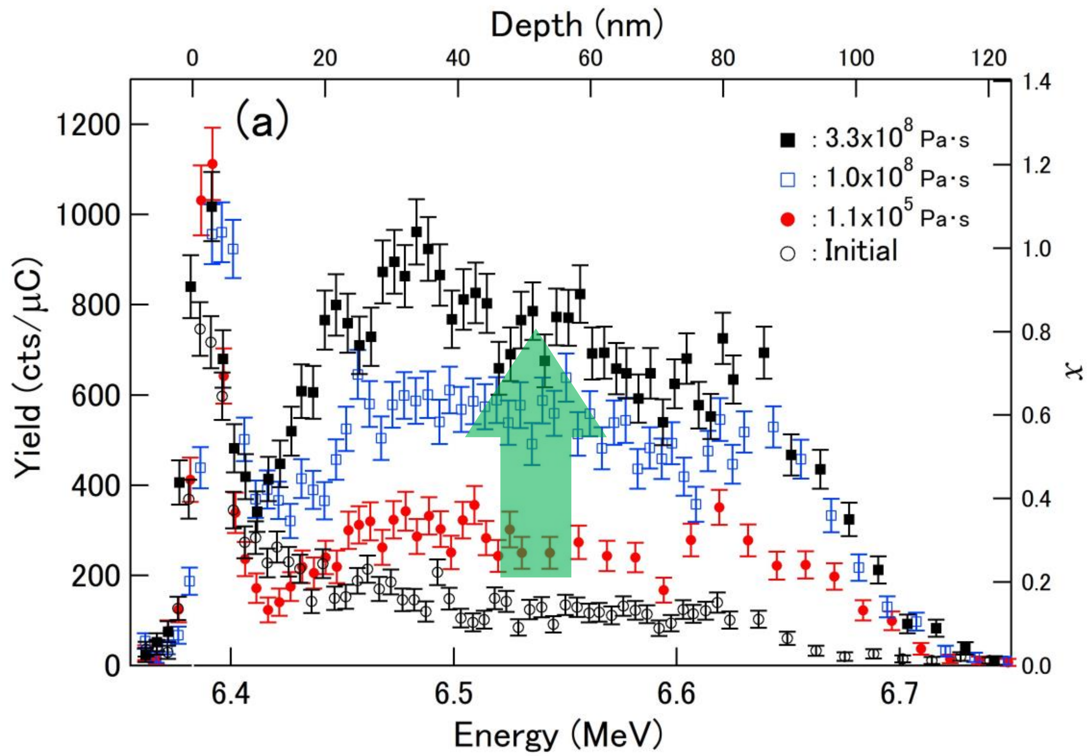
No adsorption with H_2

= Activation barrier
for H_2 dissociation

K. Takeyasu et al., JCP 140, 084703 (2014);
S. Ogawa et al., PRB.96, 085303 (2017)

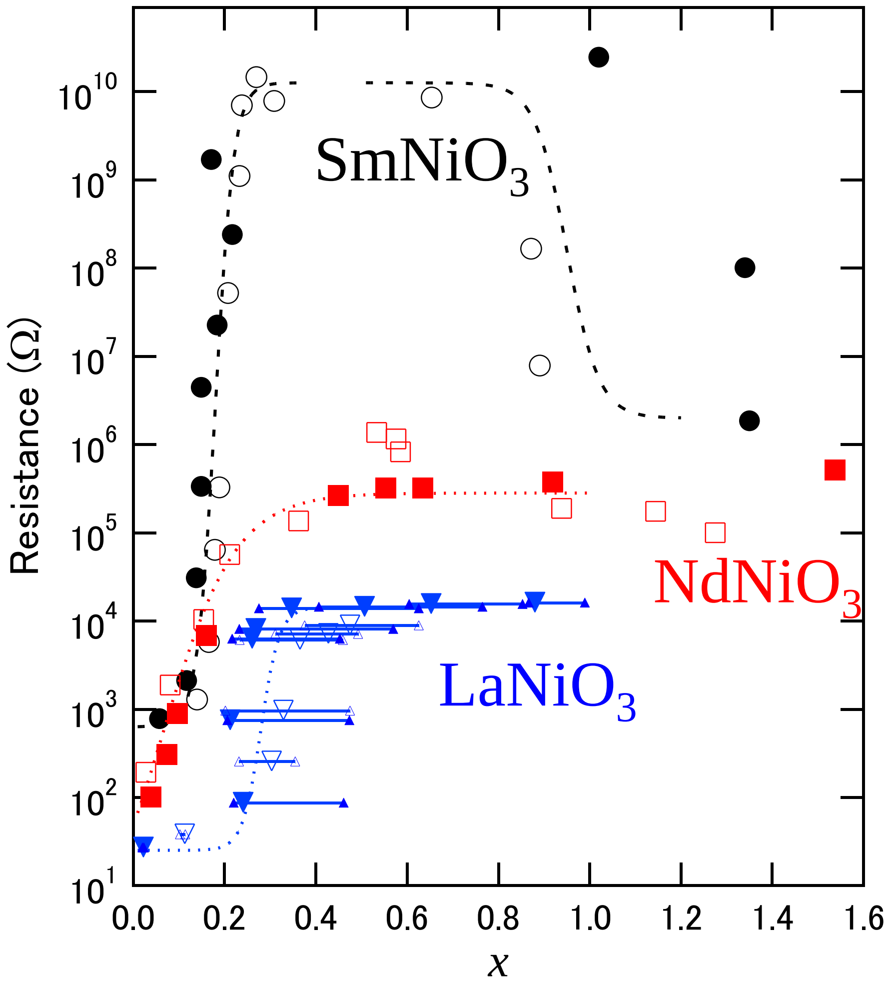
ReNiO$_3$ (Re=Sm, Nd, La)

Pt (20nm) / SmNiO$_3$H$_x$ (70 nm) / LaAlO$_3$

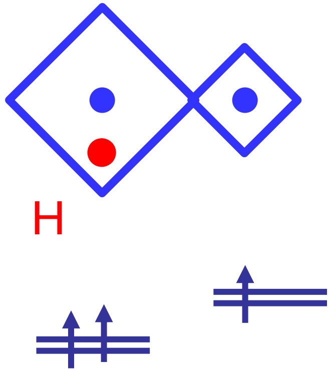


Hydrogen concentration (x) increases almost uniformly up to x~1

(Phys. Rev. Mater. 7, 085003 (2023))



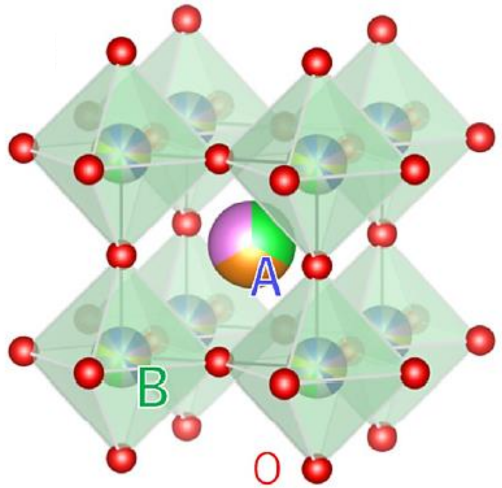
x=0.5



Site-selective Mott insulator

H–induced metal-to-insulator transition

High-entropy perovskite oxide (HEPO)



High entropy ABO$_3$

A: Ca, Sr, Ba

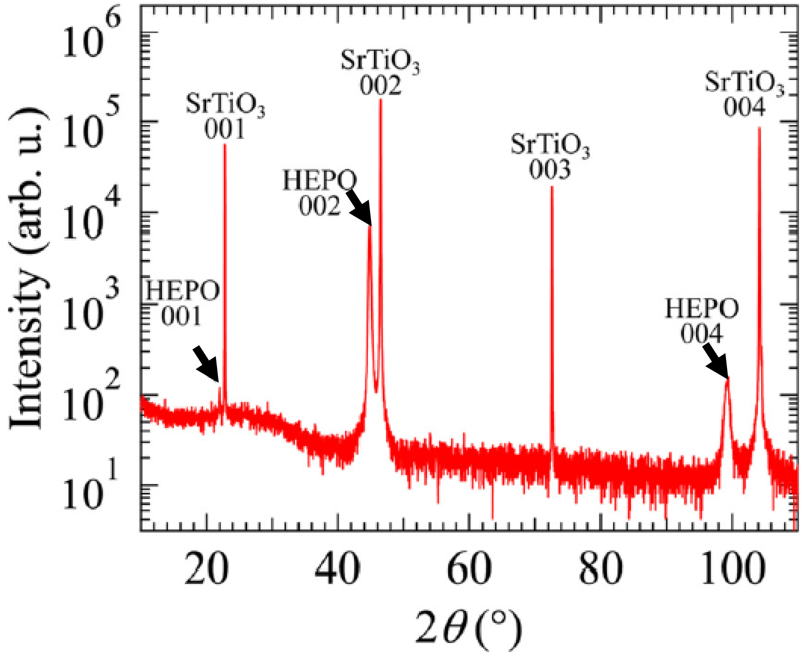
B: Si, Ti, Cr, Mn, Fe, Co, Ni, Ge, Zr, Sn, Ce, Hf

15 cations in ABO$_3$

Pulsed laser deposition on $SrTiO_3$(001)

T=873 K, P(O_2)=0.13 Pa
Thickness=90 nm

XRD
$(\theta - 2\theta)$



ICP-MS
(compositional analysis)

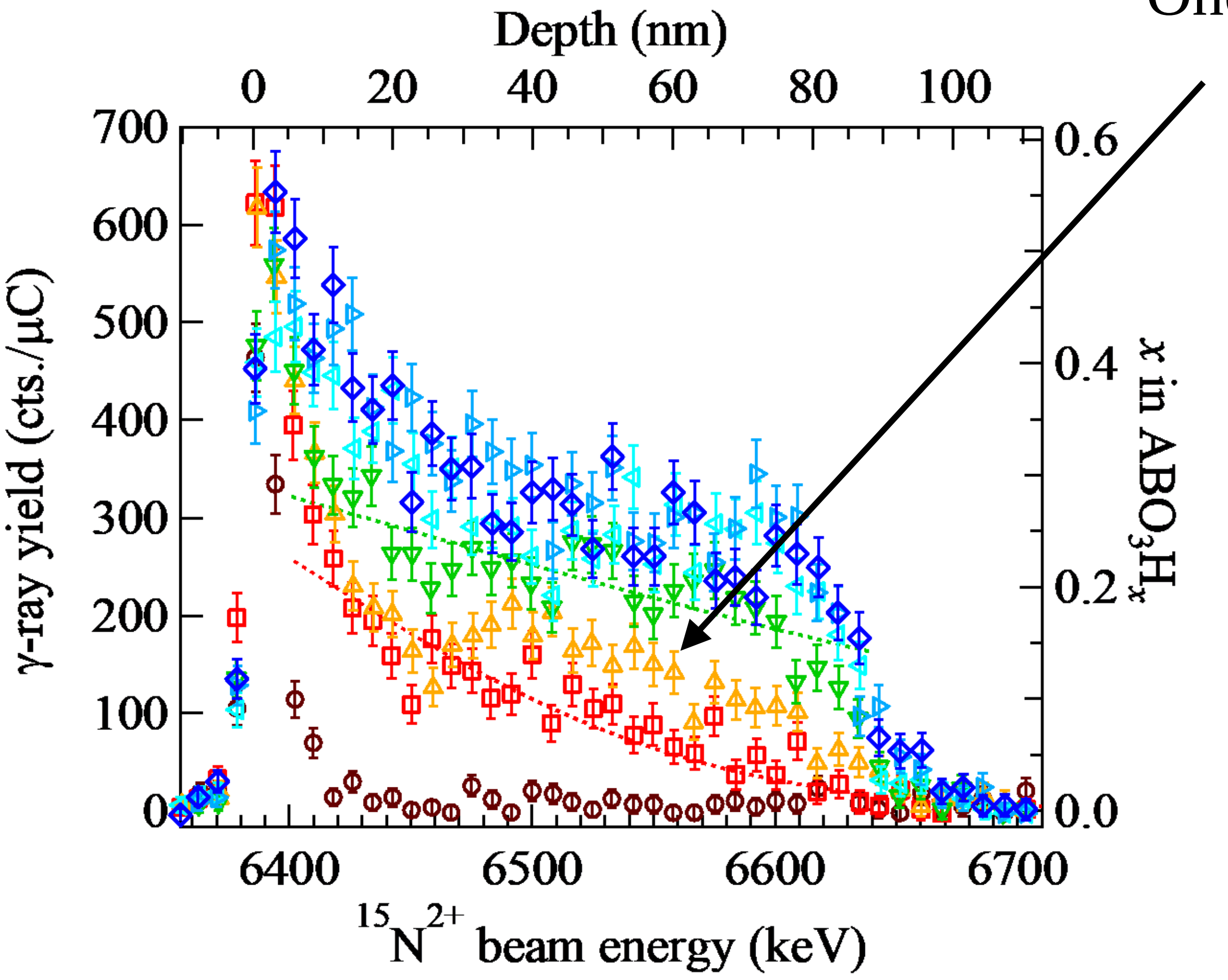
3 elements

A site		
Ca	Sr	Ba
0.305 ± 0.008	0.111 ± 0.011	0.097 ± 0.008

B site		
Si	Ti	Cr
Not detected	0.162 ± 0.038	0.028 ± 0.005
Co	Ni	Ge
0.022 ± 0.005	0.021 ± 0.006	0.018 ± 0.002
Ce	Hf	
0.014 ± 0.005	0.013 ± 0.009	
Mn	Fe	
0.025 ± 0.005	0.045 ± 0.006	
Zr	Sn	
0.116 ± 0.022	0.021 ± 0.003	

11 elements

Atomic-H dosage to HEPO film



T. Ozawa et al., J. Vac. Sci. Technol. A 42, 023402 (2024)

One-dimensional diffusion $C = C_s\left(1 - erf\left[\frac{z}{2\sqrt{Dt}}\right]\right)$

Diffusion coefficients

(9.7 ± 1.5) ×10^{-15} cm^2/s at 365 K

(4.4 ± 1.3) × 10^{-14} cm^2/s at 400 K

Activation barrier (0.54 ± 0.13) eV

(cf.) H in $NdNiO_3$: 0.39-0.76 eV

ACS Appl. Electron. Mater. 4 (2022) 4849.

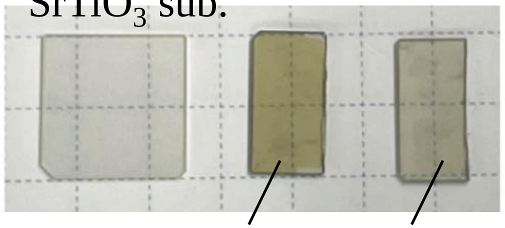
- Resistance

R > 100 MΩ after hydrogenation

- Optical images

The film gets transparent.

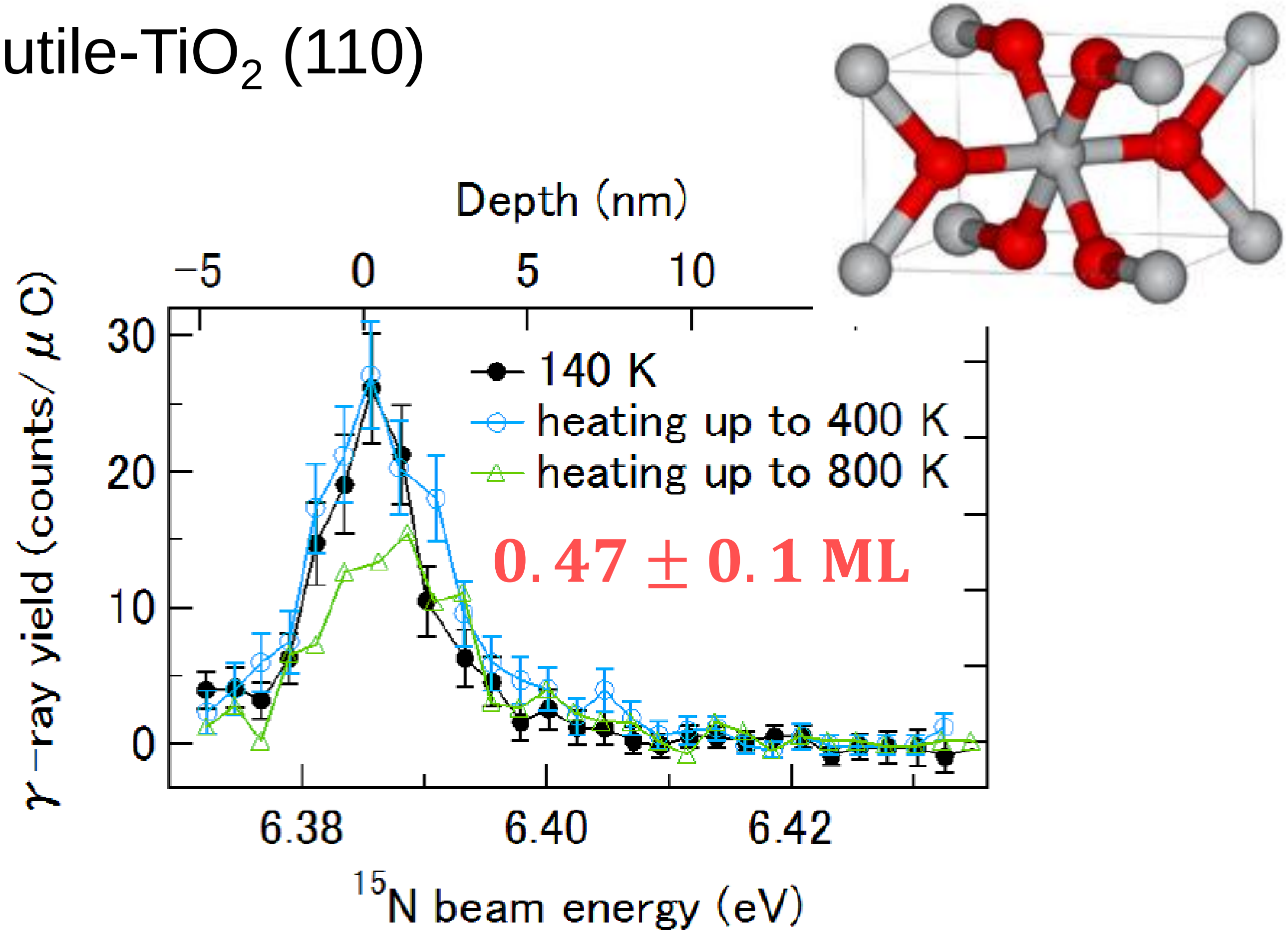
$SrTiO_3$ sub.



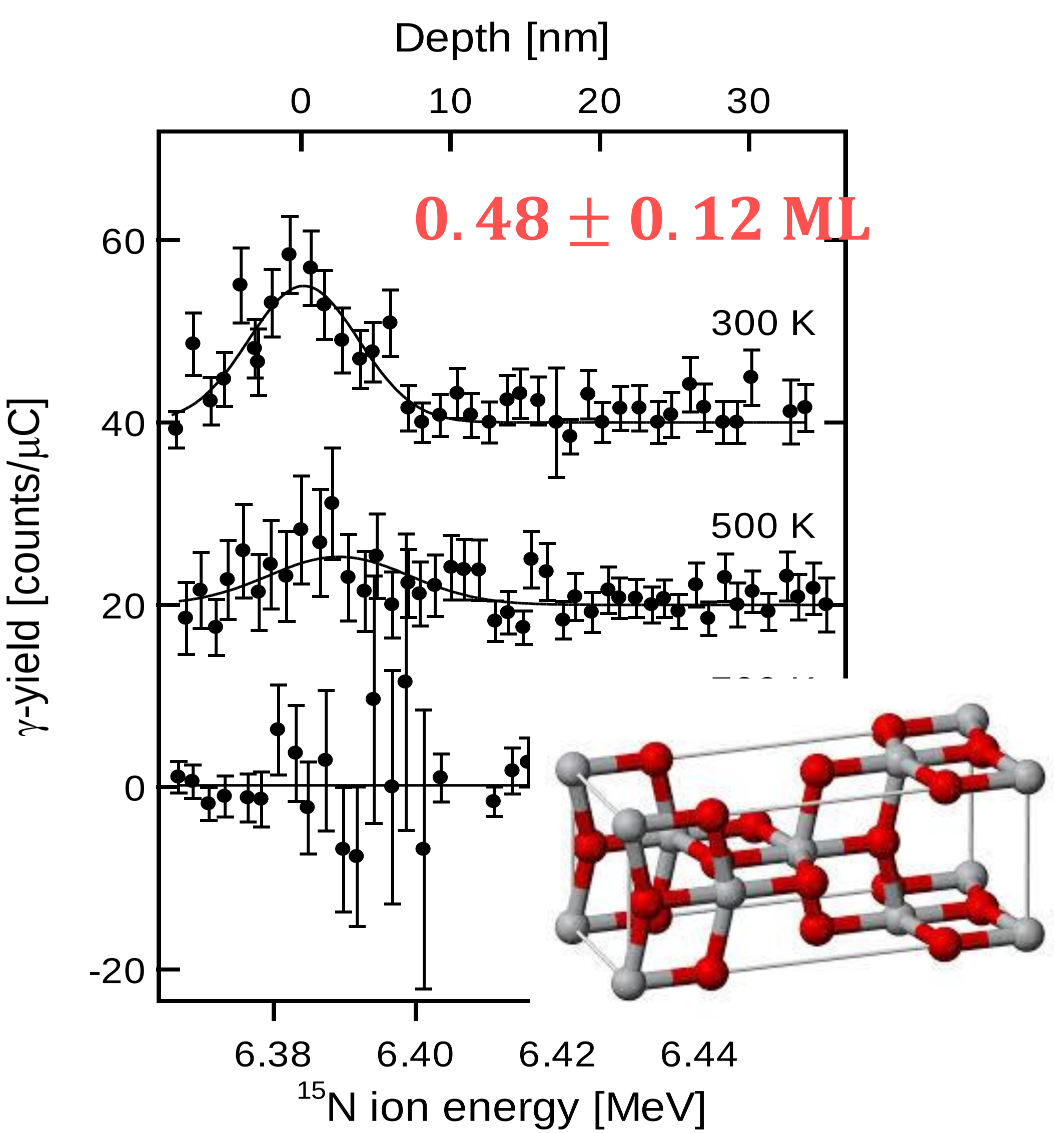
HEPO H-HEPO

Atomic H dosage to TiO_2

rutile-TiO_2 (110)



anatase-TiO_2 (101)

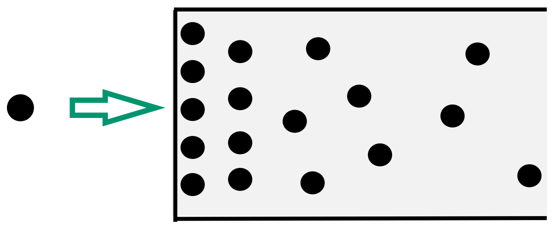


Surface adsorption & little absorption

K. Fukada et al., JPSJ 84, 064716 (2015); PRB 105, 045424 (2022)

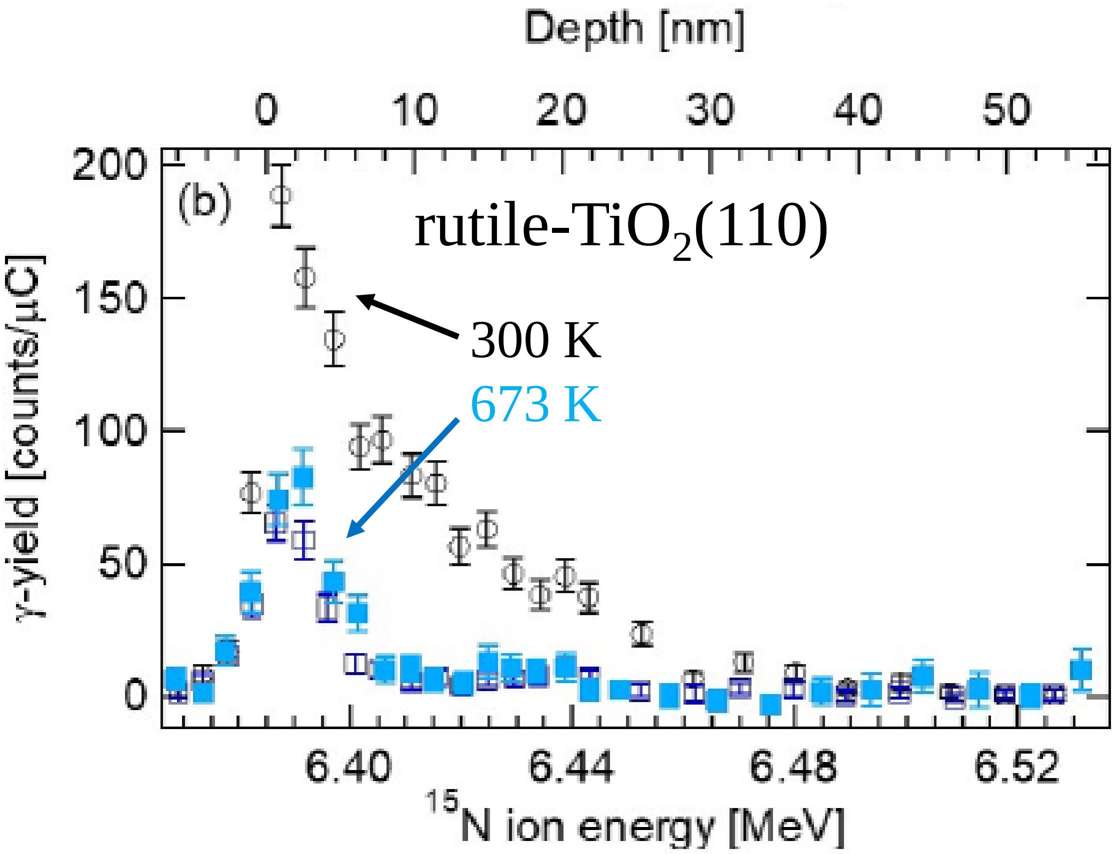
H Depth profile: diffusion analysis in TiO_2

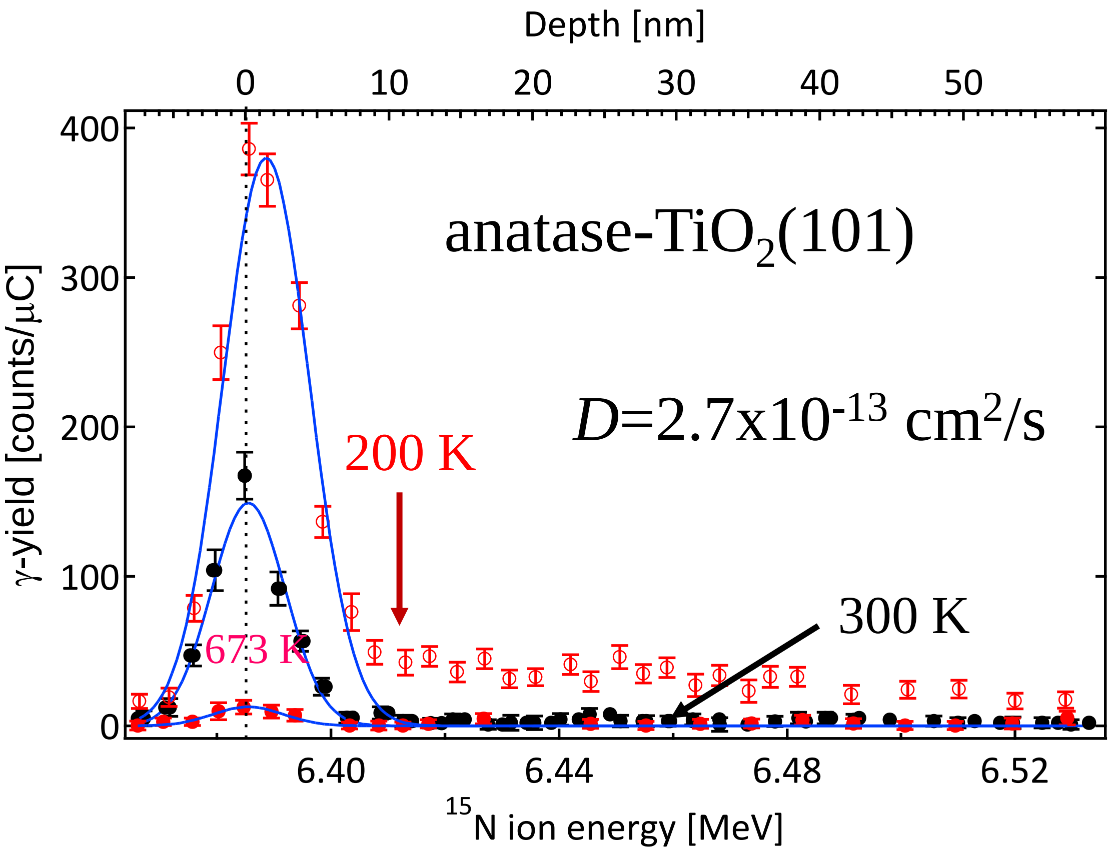
H ion Irradiation at 500 eV



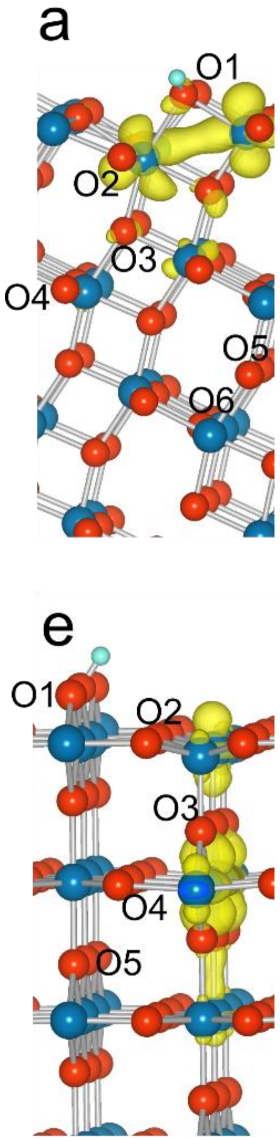
$$c(z,t)=\frac{c_0}{2}\left[1-\mathrm{erf}\left(\frac{z}{\sqrt{4Dt}}\right)\right]$$

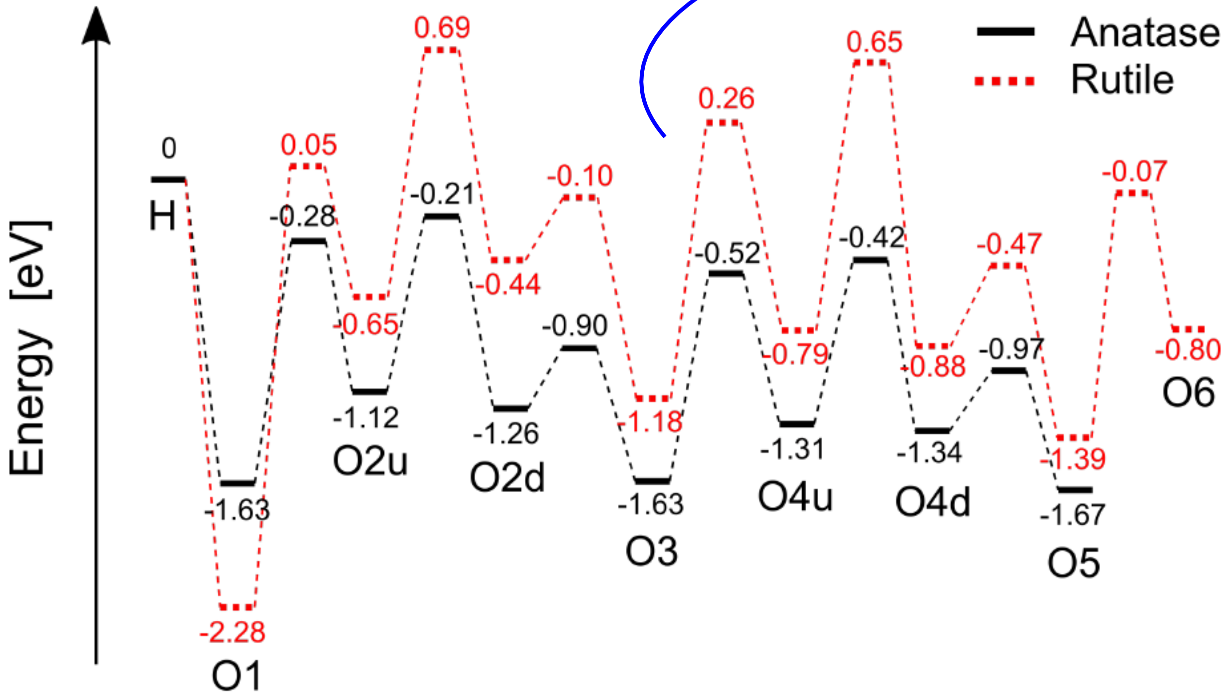
Rutile: E_a=0.86 eV
Anatase: E_a=0.21 eV



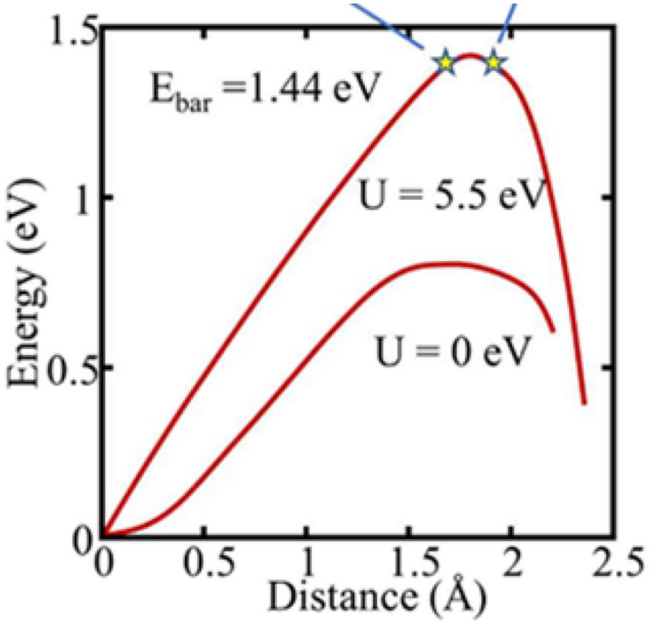


DFT: energy diagram





Rutile



Rutile: E_a=1.83 eV

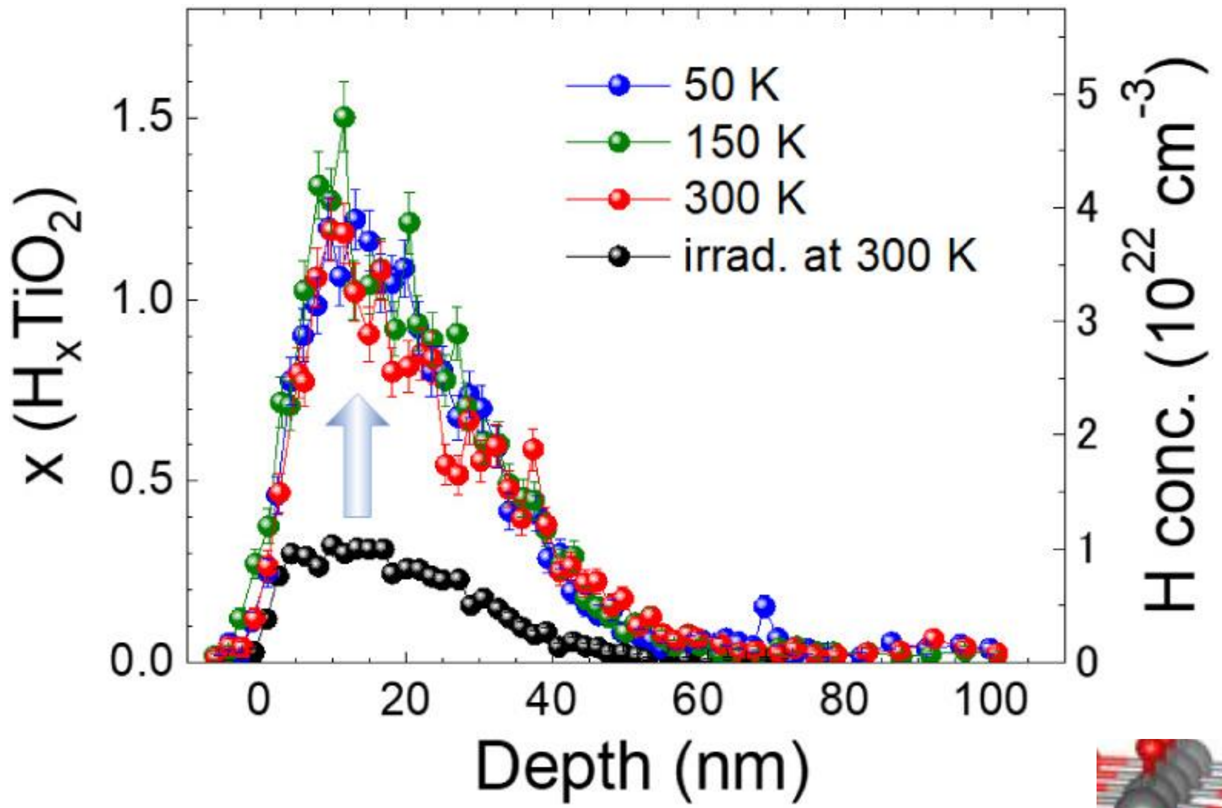
Anatase: E_a=1.21 eV

JPCC_128_8188

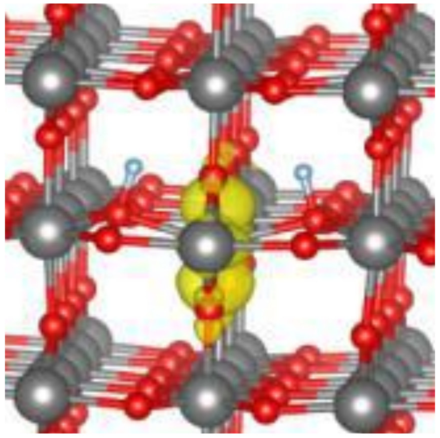
U=0: polaron gets large

Electron localization is important

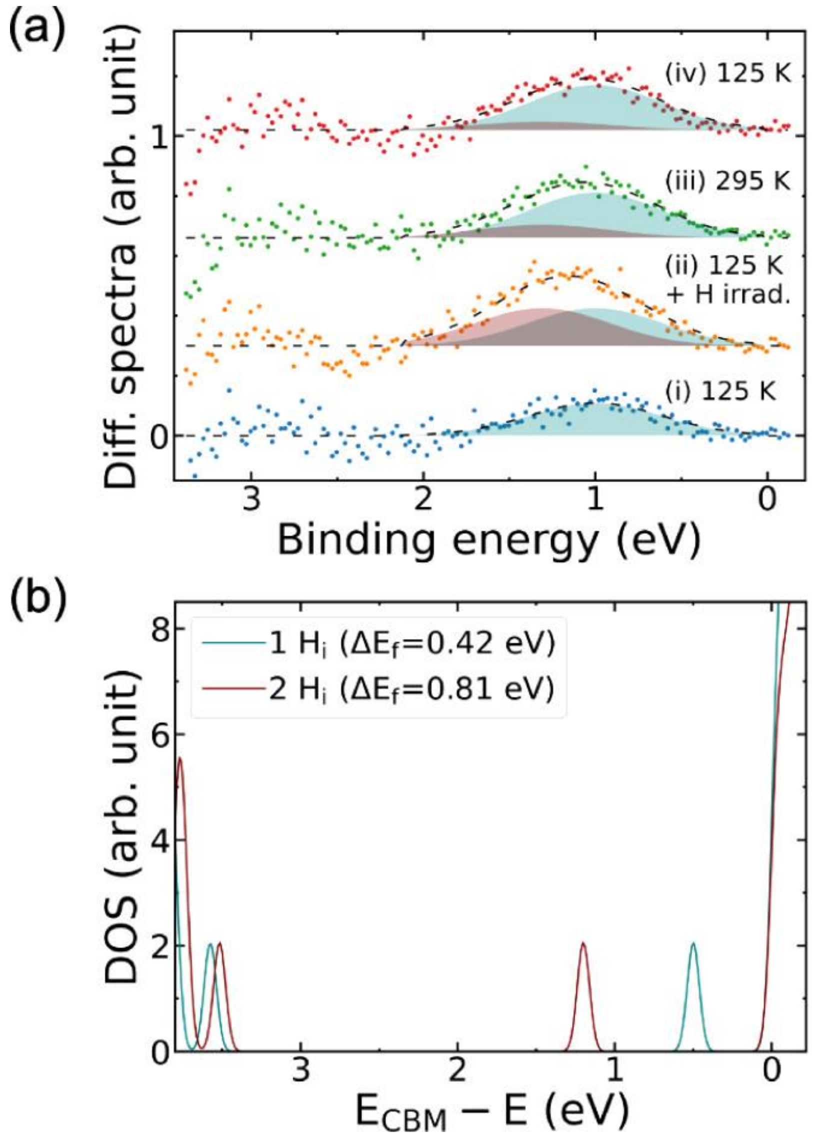
Hydrogen ion irradiation at low *T*



H concentration: TiO_2H_x (x=1.2)



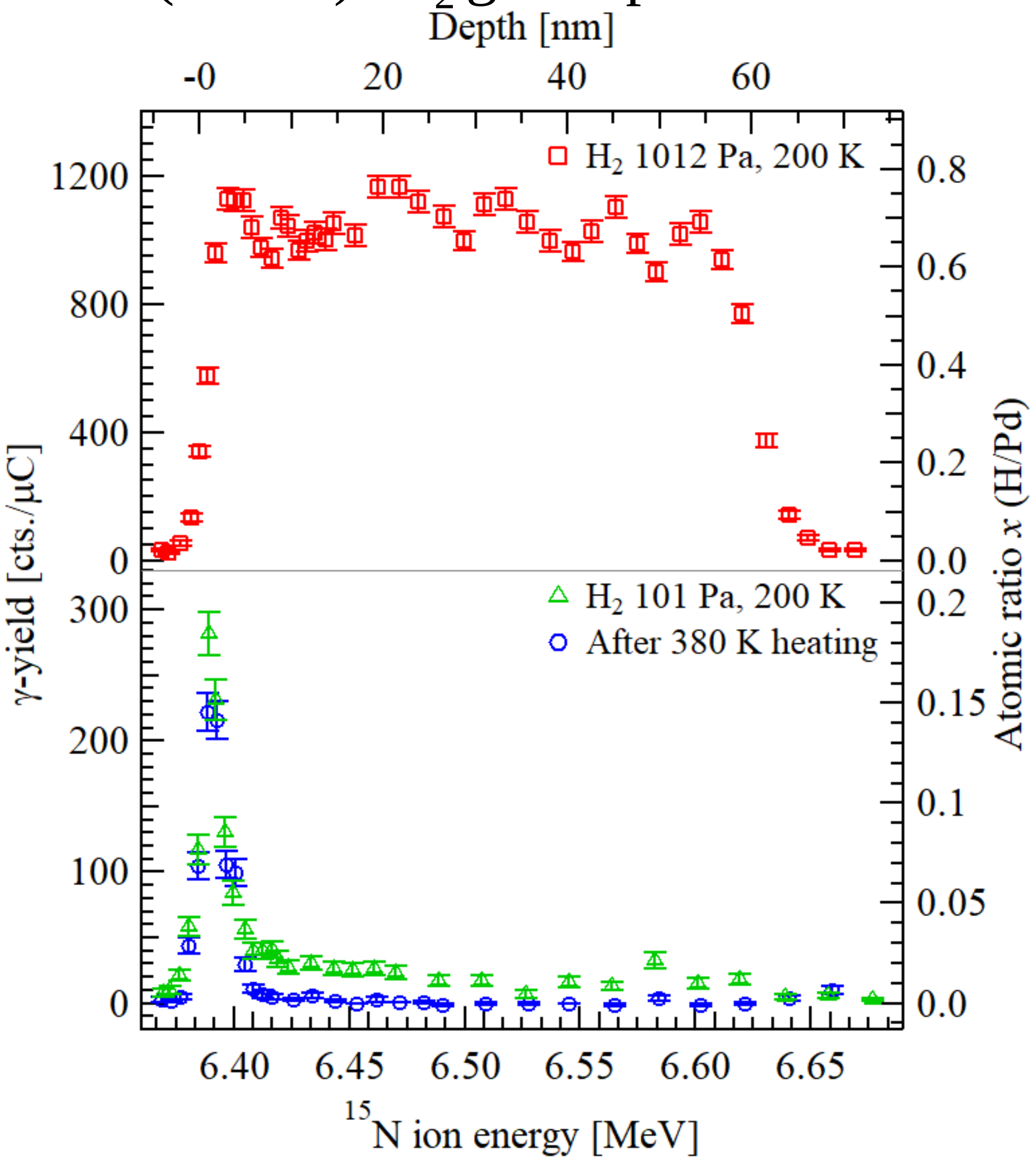
Photoemission spectroscopy



J. Am. Chem. Soc. 146, 32013 (2024)

Pd: H_2 gas exposure and ion irradiation

Pd film (60 nm): H_2 gas exposure



H ion irradiation of 0.5-2 keV at ~50 K

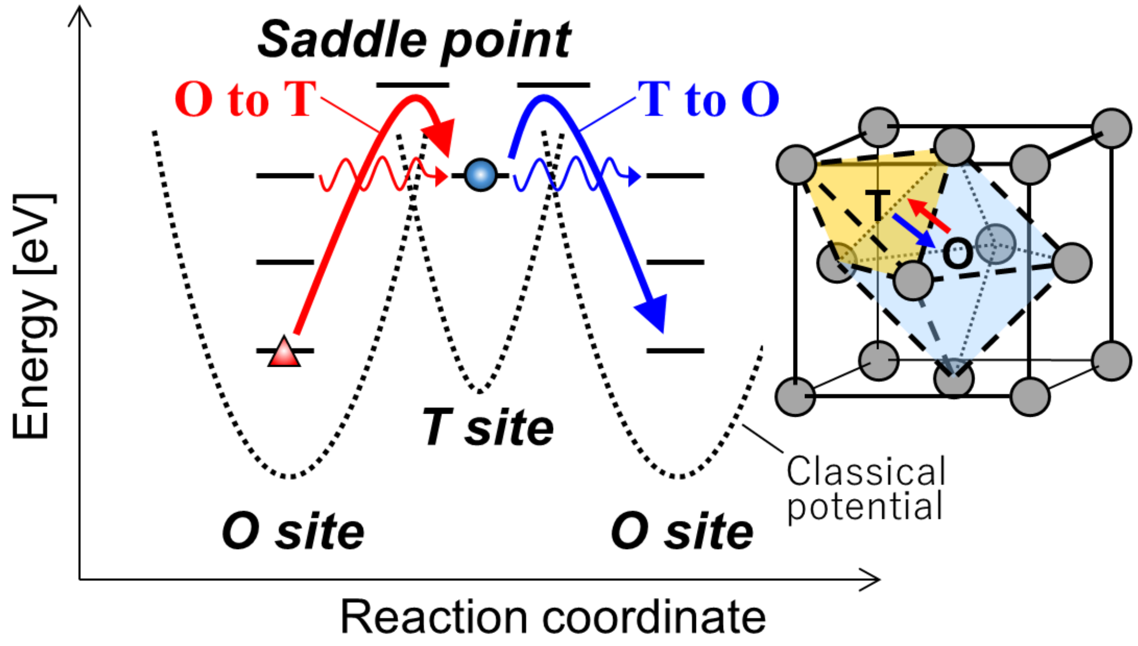
Pd(100) crystal

Partial occupation of metastable T site

E=6.42MeV:
depth~10nm

Line scan

Before & after annealing at 80 K

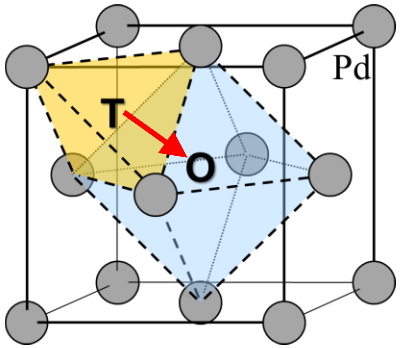


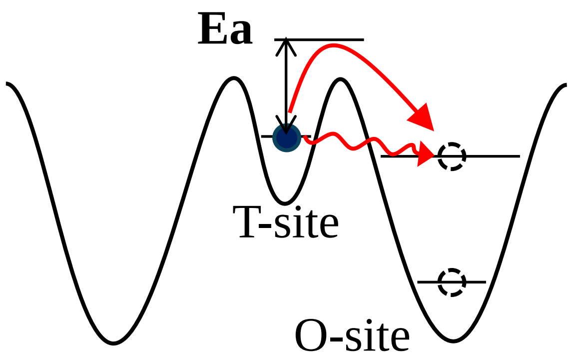
Shallow dip at <100>:

- O (50%) and T (50%)
- Move from T to O at 80 K

Temperature dependence of hopping rate

H/Pd : ~0.14





① T>80 K: Arrhenius

Thermal over-barrier

③ T<30 K: nearly T-indep

Quantum tunneling

② 80 K>T>30 K: slightly T-dependent

Phonon-assisted tunneling

✓Dressed electron
electron-proton coupling

T. Ozawa et al., JVSS 62 (2019) 492; submitted.

Summary

Hydrogen (atom and ion) interaction with metal oxides and metals

Characterization by NRA

1. Metal oxides

$SrTiO_3$: surface adsorption — insulator → metal

$ReNiO_3$: adsorption + in-diffusion — metal → Insulator

HEPO: adsorption + in-diffusion — remain insulating

TiO_2 : near-surface accumulation by H ion irradiation

faster diffusion in anatase than rutile due to polaron effects

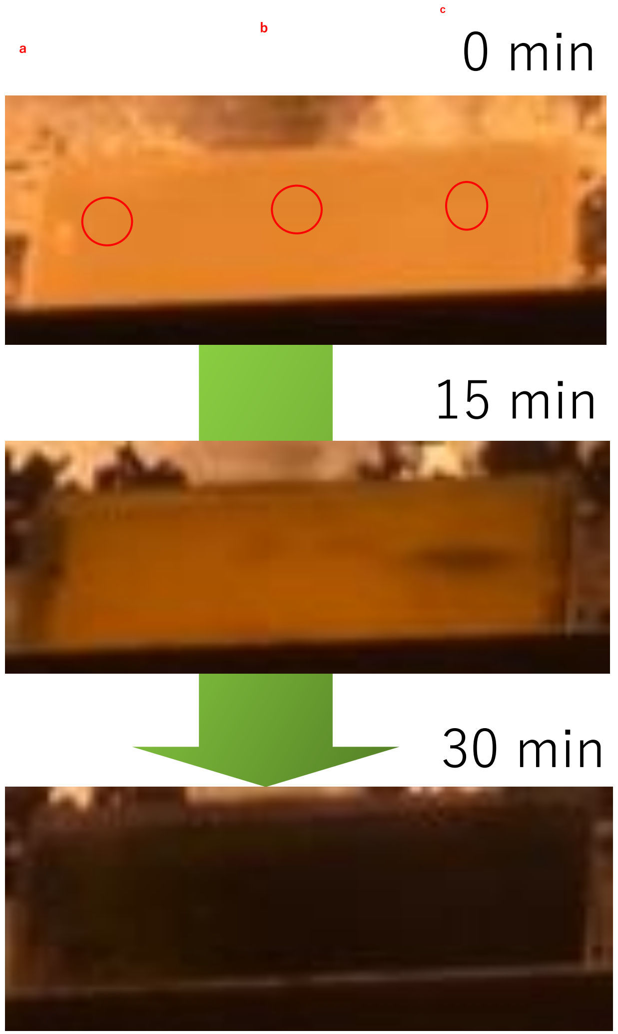
2. Metals

Metastable hydride formation by H ion irradiation,

Pd: T(50%) and O(50%) site occupation

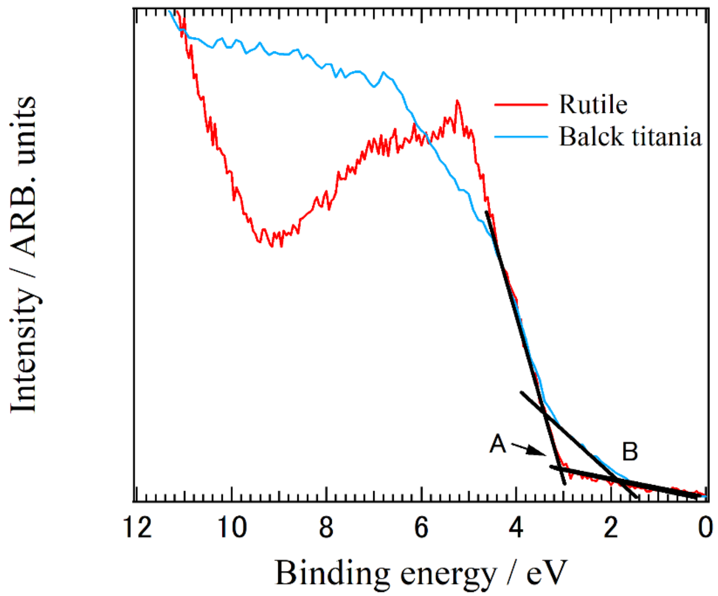
Pt: mostly stable T site occupation

Atomic H dose at high T

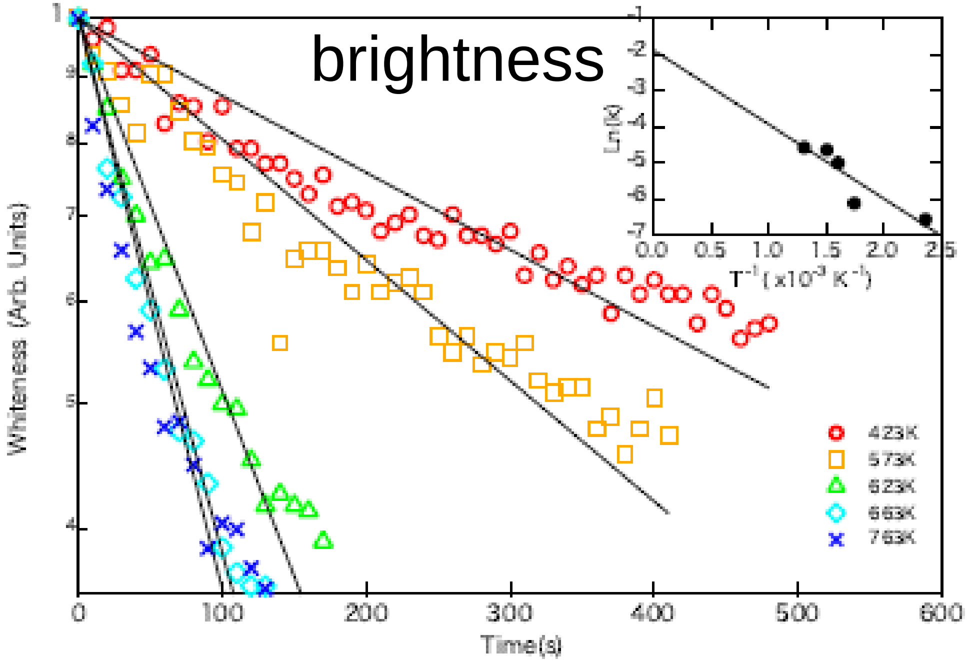


Color change to black

Substantial reduction



Temperature dependence



VBM~band gap

w/o H: 3.36 eV

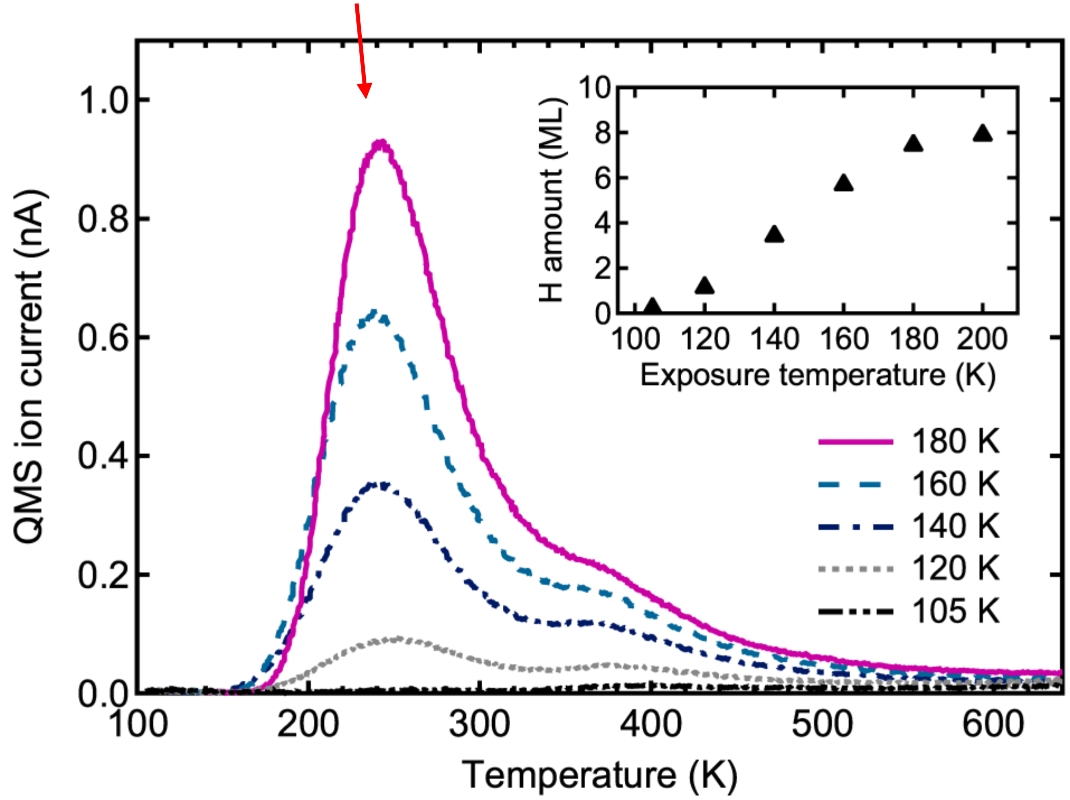
w/ H : 1.88 eV

M. Fujimoto et al., RSC Adv. 11, 4270 (2021)

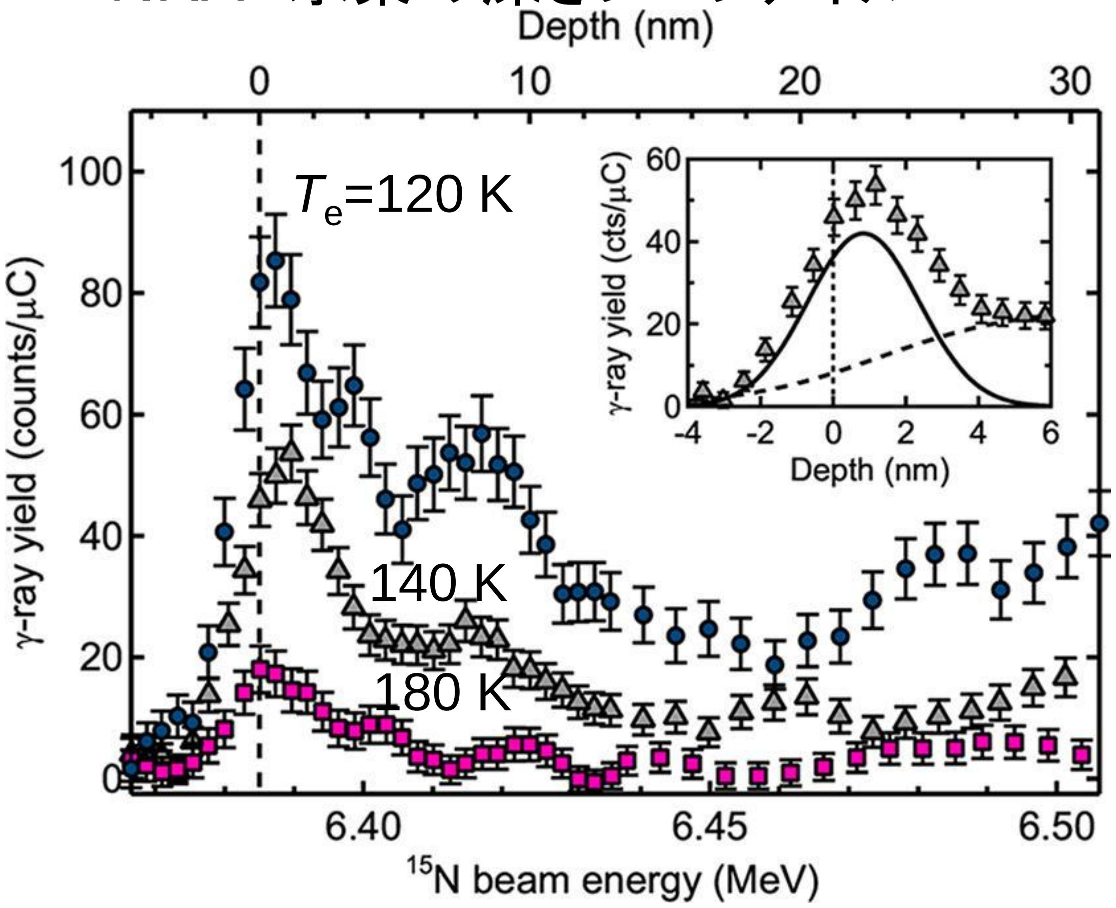
水素吸蔵材料：本当に吸蔵しているか？

$Au_{0.3}Pd_{0.7}$合金

H_2 熱脱離分光

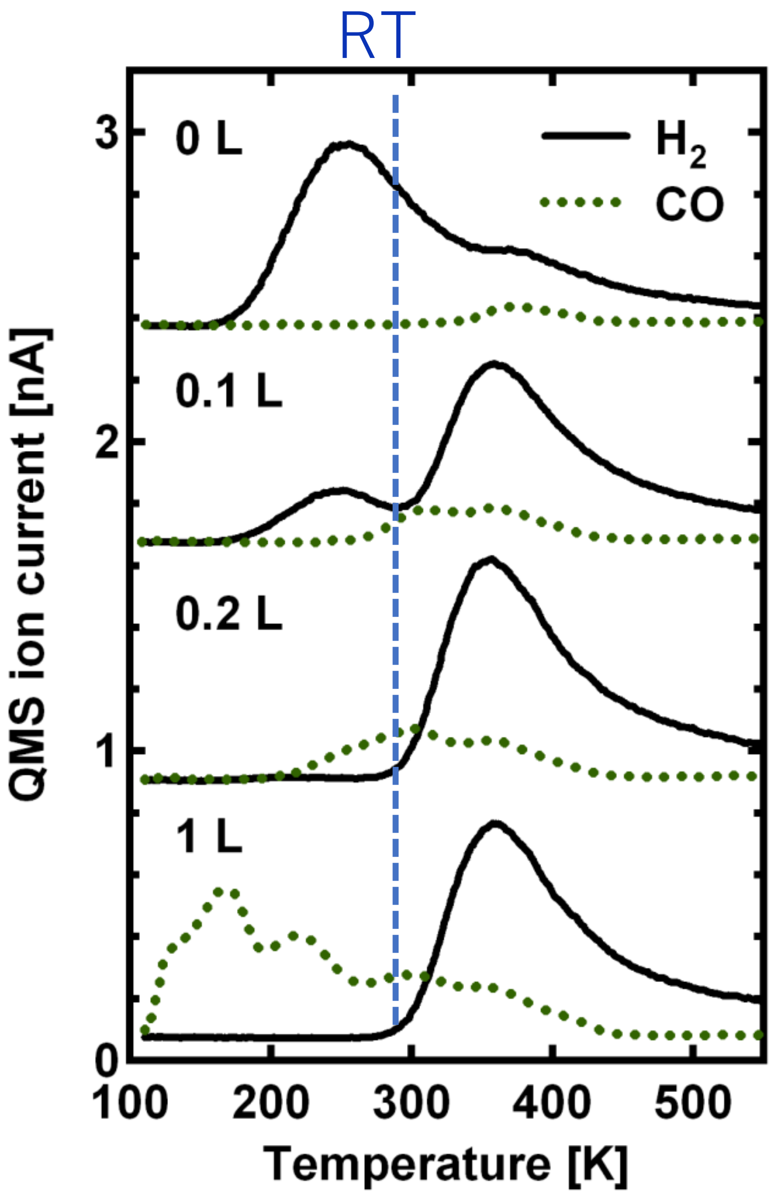


NRA　水素の深さプロファイル

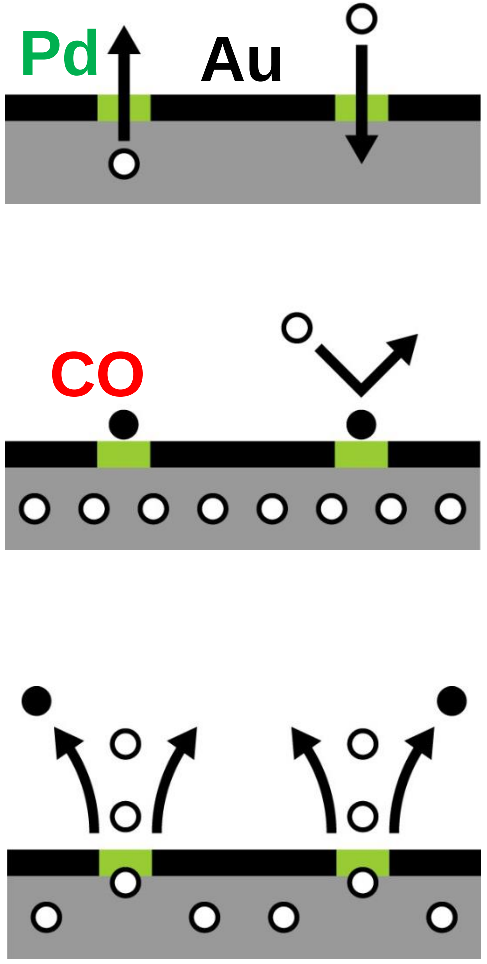


(S. Ogura et al., J. Phys. Chem. C 117, 9366 (2013))

表面で放出温度を制御する$Au_{0.3}Pd_{0.7}$(110)



Molecular cap by CO



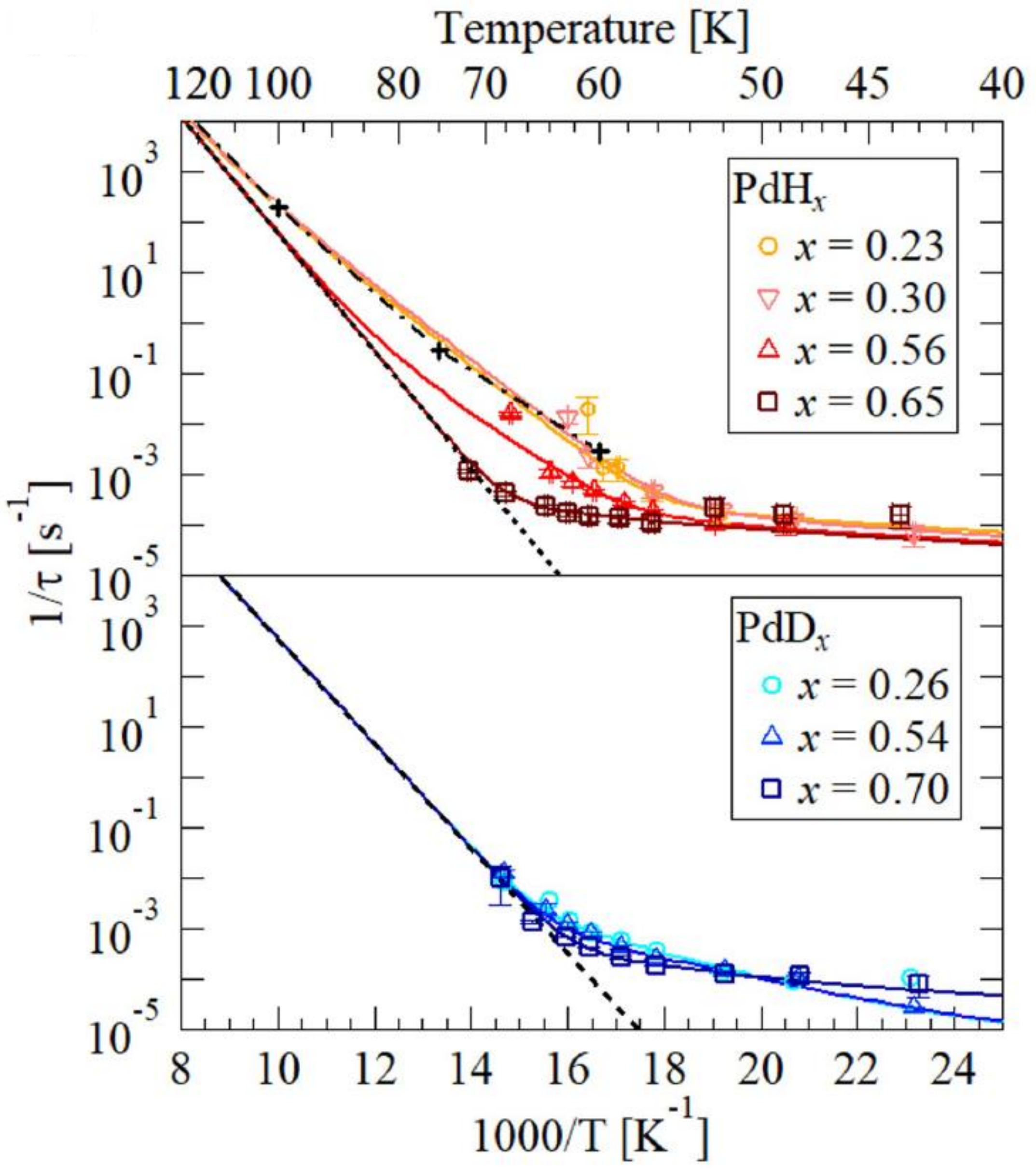
As prepared:
H_2 desorption via Pd below RT
(H does not like gold)

Cap with CO
stabilize H in bulk

Remove CO
H_2 desorption

(JPCC 117, 9366 (2013), JPCC 121, 3373 (2017); PNAS 115, 7896 (2018))

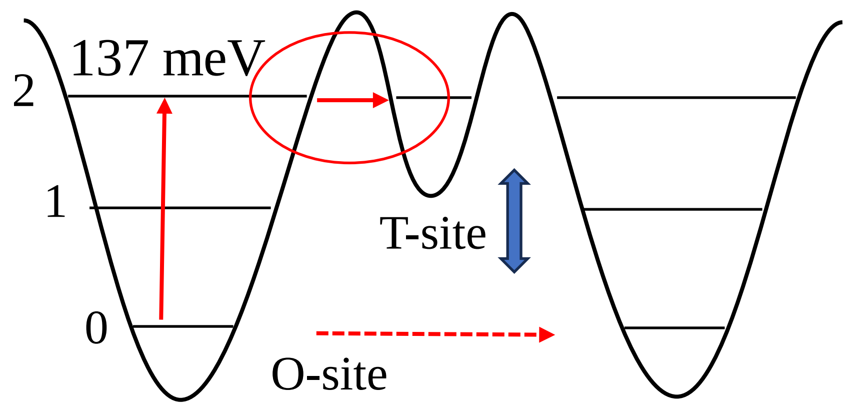
H diffusion: classical to quantum crossover



熱拡散　$\nu_0 \exp(-\frac{E_a}{kT})$

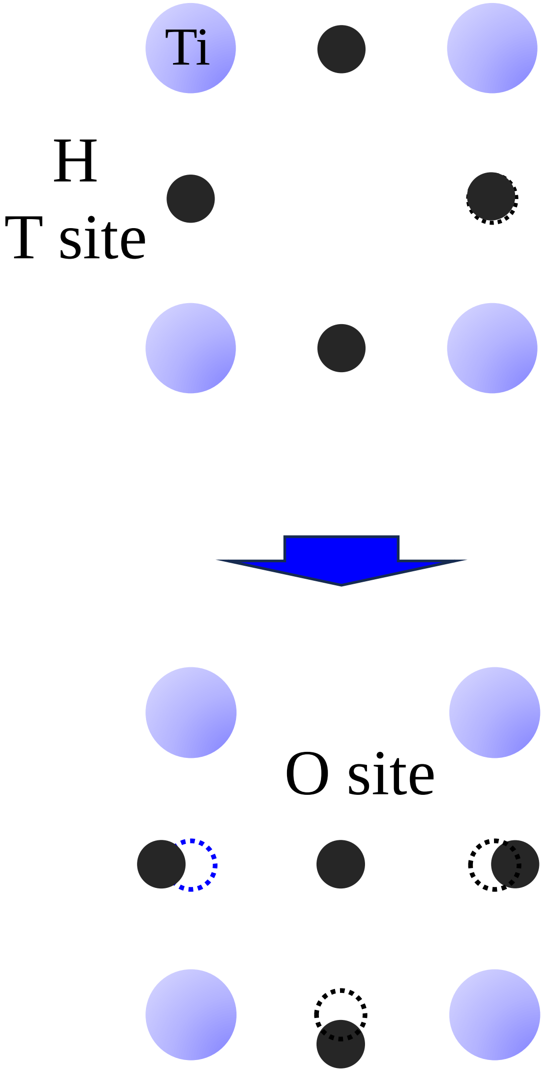
振動励起トンネル拡散　$\nu_1 \exp(-\frac{E_1}{kT})$

トンネル拡散　$\nu_3 T^{\alpha}$

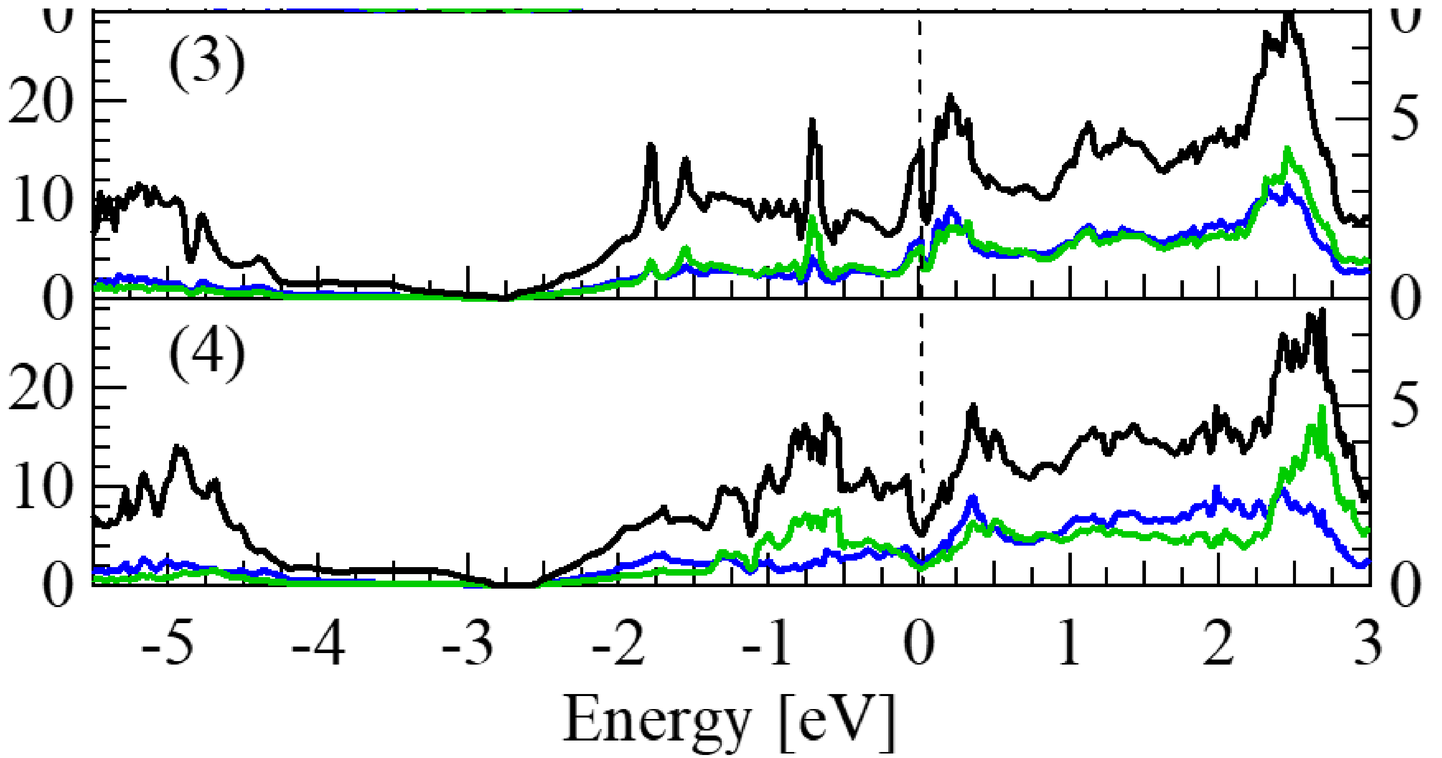


(T. Ozawa et al., J. Phys. Chem. Solids 185, 111741 (2023))

Effects of O site occupation



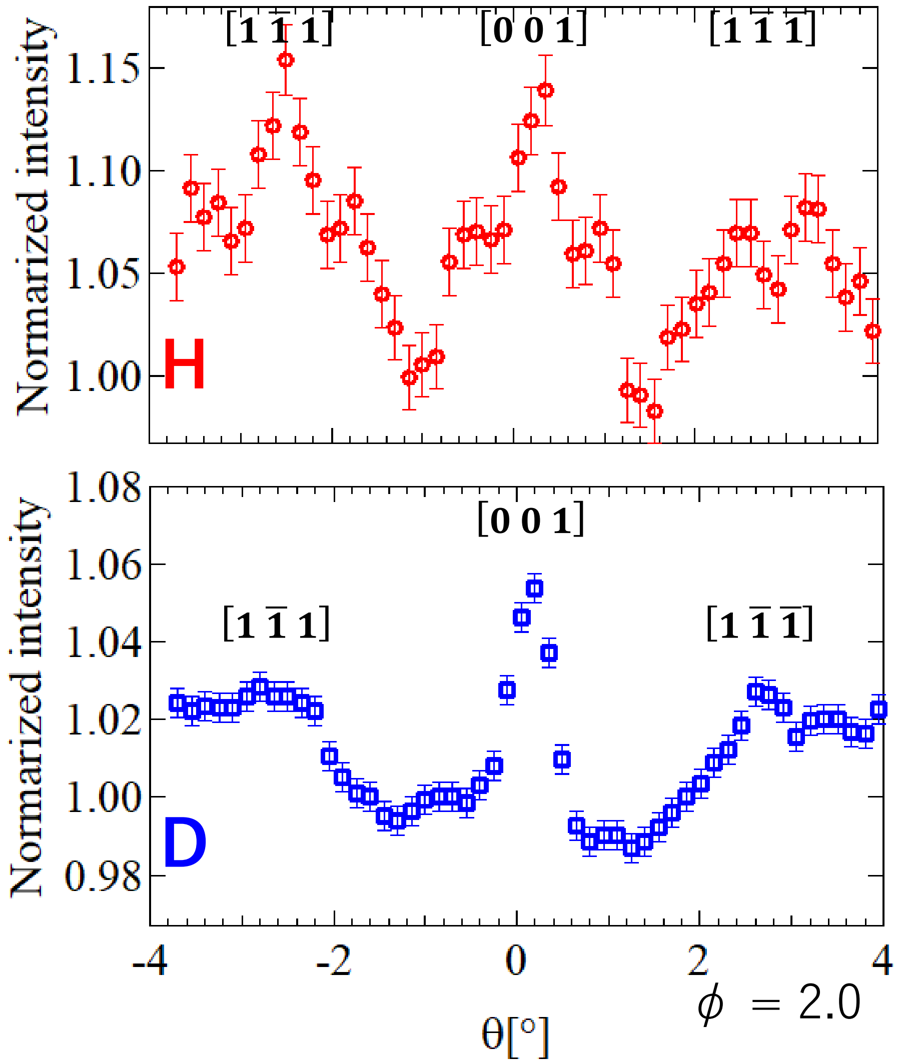
DOS by DFT



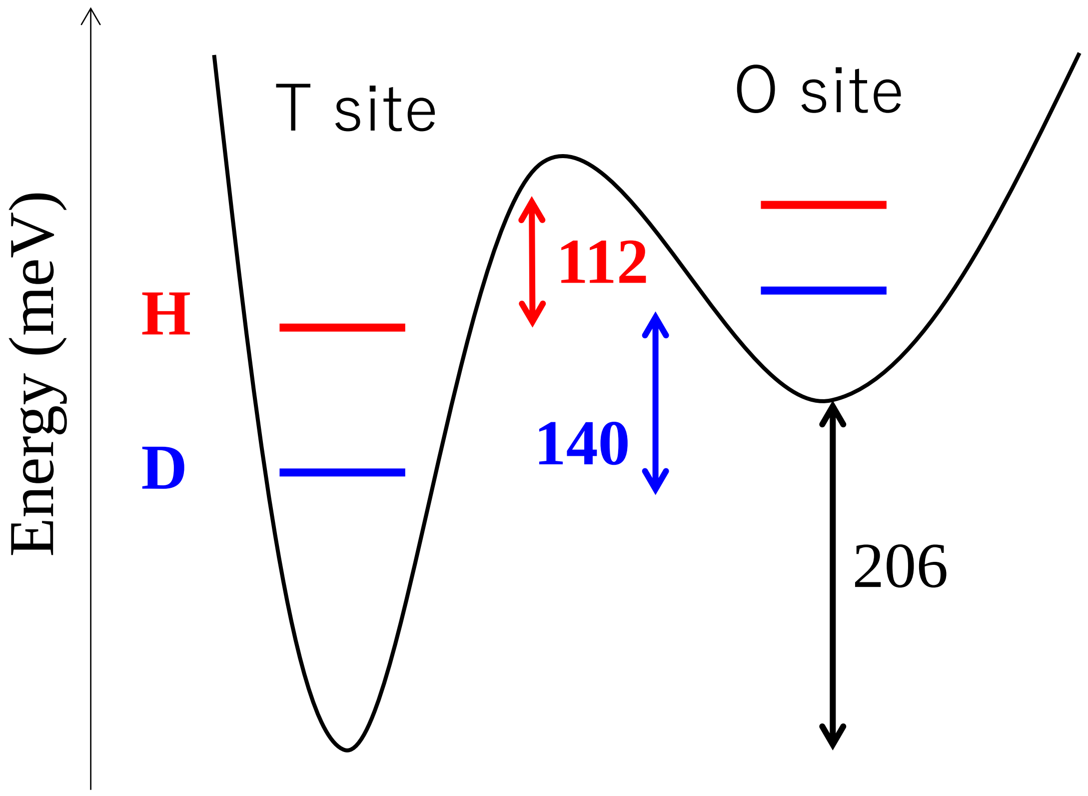
- Further split of DOS due to symmetry lowering (=H Jahn-Teller effect)
- Slight shift (0.2 Å) of H location at the T site

Isotope effect: effects of ZPE

$TiH_{0.6}D_{1.25}$ (110) (100 nm) /MgO(110)



$$ZPE = \frac{1}{2}\hbar\sqrt{\frac{k}{m}} \quad \text{(1D)}$$



D exclusively occupies the T site
because of the zero-point vibration effect.