Assessment and modeling of trap effects on hydrogen diffusivity in tungsten

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1. Hydrogen diffusivity in W
   ✓ Migration paths for H
   ✓ Modeling of migration with transition state theory (TST)
     ✓ Model validation with “H in Fe”
   ✓ Kinetic Monte Carlo simulation for trap effects
   ✓ Overall comparison with available experimental results

   (Frauenfelder) \[ D = 4.1 \times 10^{-7} \exp(-0.39 \, eV/k \, T) \]

   (Heinola; high-T data fitting) \[ D = 1.58 \times 10^{-7} \exp(-0.25 \, eV/k \, T) \]

2. Rate theoretical model for vacancy trap effects on hydrogen diffusivity

3. Experimental studies in SNU
1. H diffusivity in bcc-W: review of experimental data

\[ D = 4.1 \times 10^{-7} \exp(-0.39 \, e \, V / k \, T) \]

1. H diffusivity in bcc-W : diffusion mechanisms

✓ Stable site for hydrogen atom is tetrahedral sites. (T-site)
  - ● : W
  - ○ : T-site (of interest)
  - ● : 1\textsuperscript{st} neig. T-site
  - ● : 2\textsuperscript{nd} neig. T-site

✓ Migration to the 1\textsuperscript{st} neighboring T-site passes Trigonal site (○).
✓ Migration to the 2\textsuperscript{nd} neighboring T-site passes Octahedral site (O-site; ○).

Migration via trigonal-site (to a 1st-neighboring T-site)

Migration via octahedral-site (to a 2nd-neighboring T-site)
1. H diffusivity in bcc-W: transition state analysis

The migration via Trigonal-site ($E_m=0.20-0.21$ eV [1.2]) is the minimum-barrier path, and thus is the most probable migration path for H [1,2].

Although the migration via Octahedral-site ($E_m=0.40$ eV [3]) gives a closer barrier to the experiment, it should be inappropriate.

1. H diffusivity in bcc-W: expression of diffusion coefficient

$$D = \frac{1}{6} f d^2 \Gamma$$

- $D$ [m$^2$/s]: diffusion coefficient
- $f$: correlation factor
  - F=1 as no correlation in sequential jumps.
- $d$ [m]: jump distance
  - $d = a_0 / 2\sqrt{2} = 1.12$ Å
- $\Gamma$ [1/s]: jump frequency

$$\Gamma = nve^{-\frac{\Delta E}{kT}}$$

- $n$: the number of equivalent paths
  - $n = 2$ or $4$
- $v$ [1/s]: jump attempt frequency
- $\Delta E$ [eV]: migration barrier

Migration via trigonal-site (to a 1st-neighboring T-site)
1. H diffusivity in bcc-W: determination of $\nu$ and $\Delta E$ by TST

(1) Classical transition state theory (TST) with harmonic approx. by Vineyard*.

\[ \Delta E = E_{Tri-site} - E_{T-site} \]

\[ \nu_{Vine} = \left( \prod_{i=1}^{N} \nu_i \right) / \left( \prod_{i=1}^{N-1} \nu'_i \right) \]


(2) Classical TST with quantum mech. partition functions within harmonic approx.

\[ \Delta E = E_{Tri-site} - E_{T-site} \]

\[ \nu_{qHTST} = \frac{kT}{\hbar} \times \left\{ \prod_{i}^{N-1} \left( \frac{\exp\left(-\frac{\hbar \nu'_i}{2kT}\right)}{1 - \exp\left(-\frac{\hbar \nu'_i}{kT}\right)} \right) / \prod_{i}^{N} \left( \frac{\exp\left(-\frac{\hbar \nu_i}{2kT}\right)}{1 - \exp\left(-\frac{\hbar \nu_i}{kT}\right)} \right) \right\} \]

(3) Explicit correction of zero-point energies to the Vineyard model

\[ \Gamma_{ZPE} = \nu_{Vin}^* \exp \left( - \frac{\Delta E + E_{ZPE}}{RT} \right) \]

\[ E_{ZPE} = \frac{1}{2} \sum_{i=1}^{N-1} h\nu'_i - \frac{1}{2} \sum_{i=1}^{N} h\nu_i \]
1. H diffusivity in bcc-W: application to “H in W” with DFT results

- DFT calculation was done with VASP code using PBE functional.

1. H diffusivity in bcc-W: Heinola’s suggestion


(Frauenfelder) \[ D = 4.1 \times 10^{-7} \exp(-0.39 \, eV / k \, T) \]

(Heinola; high-T data fitting) \[ D = 1.58 \times 10^{-7} \exp(-0.25 \, eV / k \, T) \]
1. H diffusivity in bcc-W: summary of available experimental data

(Original: Eq. 1) \[ D = 4.1 \times 10^{-7} \exp(-0.39 eV/kT) \]

(High-T only: Eq. 2) \[ D = 1.58 \times 10^{-7} \exp(-0.25 eV/kT) \]
1. H diffusivity in bcc-W: Kinetic Monte Carlo (KMC) method

KMC simulation pursues a system evolution by repeating some atomic-scale kinetic events which are relevant with a phenomenon of interest. Judgment whether an event attempt will succeed or fail is made using Monte Carlo simulation technique.

\[ \nu_{\text{event}} = \nu_{\text{attempt}} \times p = \nu_{\text{attempt}} \times \exp\left(-\frac{E}{kT}\right) \]

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**Diagram:**

- "Trapped" state
- "Solute" state, Neighboring to V
- "Solute" state, Non-neighboring to V
- Trap event
- Detrap event
- Migration event
1. H diffusivity in bcc-W: Isn’t it too simple?
- focus on high temperature (>1100 K) of pure W + H₂ absorption-

✓ Vacancy trapping energy: (~1.4 eV)

✓ Impurities
  ✓ Non-metallic (~ 0.3 eV)
  ✓ Metallic (~0.7 eV for substitutional Fe)
    * X.S. Kong et al., J. Nucl. Mater. 433 (2013) 357;
    G.H. Lu, Nucl. Fusion 54 (2014) 086001

✓ Vacancy clustering (pre-treatment at 2400 K); V clusters are decomposed at around 1700 K

✓ Dislocation (~0.7 eV)

✓ Grain boundary (~1.1 eV)
1. H diffusivity in bcc-W: V-H interaction model

\[ E_{\text{detrap}} = E_{\text{binding}} + E_{\text{migr}} \]

1. H diffusivity in bcc-W: simplification of potential energy profile
1. H diffusivity in bcc-W: i.e. DFT results

1. H diffusivity in bcc-W: trap/detrap process

- [●: 1\textsuperscript{st} neig. O-site to vacancy] The sites for trapped H atoms
- [○: 2\textsuperscript{nd} neig. T-site to vacancy] Some sites for solute H atoms
  - Detrap event: From Red to Blue (via Green)
  - Trap event: From Blue to Red (via Green)
1. H diffusivity in bcc-W: KMC results on trap effects (vacancy)

- <pretreatment> 2400 K for 10 h in H$_2$ (8x10$^4$ Pa) and in vacuum (10$^{-4}$ Pa)
- <H-loading> 1120-2080 K in H$_2$ (8x10$^4$ Pa); 400 min at 1120 K, 60 min at 2080 K
- <Experiment> ✓ Solubility ✓ Diffusivity

✓ H concentration is set according to H solubility of Frauenfelder’s experiment.
✓ Equilibrium vacancy concentration at 2400 K (pre-treatment temperature of Frauenfelder’s experiment) is 0.01 ppm with 3.8 eV vacancy formation energy.
1. H diffusivity in bcc-W: KMC results - effects of uncertainty in DFT -
1. H diffusivity in bcc-W: KMC results
   -Influence of H/V ratio on effective diffusivity-

3 characteristic regions:
I. low H/V ratio region (H/V < 1), where apparent diffusion coefficients are almost constant;
II. intermediate H/V ratio region (1 < H/V < 100), where the apparent diffusion coefficient increases as the H/V ratio increases;
III. high H/V ratio region (H/V > 100), where effective diffusion coefficients are comparable with the true diffusion coefficient (Heinola’s equation).
1. H diffusivity in bcc-W: summary

\[ D_{\text{lower-limit}} = D \left( 1 + 4c_{\text{vacancy}} \times \exp \left( \frac{E_{\text{binding}}}{kT} \right) \right) \]

\[ E_{\text{binding}} = 1.32 \text{ eV} \]

of V1H1 complex

Appendix-1) Influence of XC-functionals of DFT calculation
Results in hydrogen related properties in W

<table>
<thead>
<tr>
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<th>LDA</th>
<th>PBE</th>
<th>PBEsol</th>
<th>AM05</th>
<th>TPSS</th>
<th>RTPSS</th>
<th>M06L</th>
<th>Exp.</th>
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<tbody>
<tr>
<td><strong>V formation (eV)</strong></td>
<td>3.330</td>
<td>3.221</td>
<td>3.397</td>
<td>3.555</td>
<td>3.710</td>
<td>3.772</td>
<td>5.037</td>
<td>3.67(^a) ± 0.2</td>
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<tr>
<td></td>
<td>(3.344)</td>
<td>(3.267)</td>
<td>(3.453)</td>
<td>(3.616)</td>
<td>(3.832)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td><strong>V migration barrier (eV)</strong></td>
<td>1.748</td>
<td>1.717</td>
<td>1.762</td>
<td>1.787</td>
<td>1.797</td>
<td>1.789</td>
<td>1.545</td>
<td>1.78(^a) ± 0.1</td>
</tr>
<tr>
<td></td>
<td>(1.756)</td>
<td>(1.722)</td>
<td>(1.760)</td>
<td>(1.783)</td>
<td>(1.786)</td>
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</table>

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<th>M06L</th>
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<tbody>
<tr>
<td><strong>Solution (eV)</strong></td>
<td>0.633</td>
<td>0.904</td>
<td>0.773</td>
<td>0.862</td>
<td>0.982</td>
<td>1.063</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.627)</td>
<td>(0.897)</td>
<td>(0.761)</td>
<td>(0.850)</td>
<td></td>
<td>(1.052)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Migration barrier (eV)</strong></td>
<td>0.206</td>
<td>0.203</td>
<td>0.207</td>
<td>0.208</td>
<td>0.214</td>
<td>0.216</td>
<td>0.233</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.205)</td>
<td>(0.203)</td>
<td>(0.207)</td>
<td>(0.208)</td>
<td></td>
<td>(0.216)</td>
<td></td>
<td></td>
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<tr>
<td><strong>V-H interaction energy (eV)</strong></td>
<td>V1-H1</td>
<td>1.243</td>
<td>1.176</td>
<td>1.249</td>
<td>1.292</td>
<td>1.289</td>
<td>1.344</td>
<td>1.567</td>
</tr>
<tr>
<td></td>
<td>(1.255)</td>
<td>(1.204)</td>
<td>(1.270)</td>
<td>(1.316)</td>
<td></td>
<td>(1.370)</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>(5.762)</td>
<td>(5.473)</td>
<td>(5.802)</td>
<td>(6.034)</td>
<td></td>
<td>(6.286)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>V1-H12</td>
<td>7.185</td>
<td>7.011</td>
<td>7.223</td>
<td>7.380</td>
<td>7.627</td>
<td>7.875</td>
<td>8.073</td>
</tr>
<tr>
<td></td>
<td>(7.027)</td>
<td>(6.881)</td>
<td>(7.029)</td>
<td>(7.183)</td>
<td></td>
<td>(7.712)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1. Hydrogen diffusivity in W

2. Rate theoretical model for vacancy trap effects on hydrogen diffusivity
   ✓ Deqiong Zhu, Takuji Oda

3. Experimental studies in SNU
2. Derivation of rate equations for V-H interaction in “H in W”

[Motivation] In KMC simulation, we simplified the potential energy profile. In this study, we construct rate equations considering changes in potential energy profile as a function of the number of trapped H. For this purpose, we study with “H in Fe”, because a good potential model is available.

2. Derivation of rate equations for V-H interaction in “H in W”
-comparison between Fe (with potential model) and W (with DFT)-

Classical MS results for Fe

DFT calculation results for W

2. Derivation of rate equations for V-H interaction in “H in W”

-Rate equations for trap and detrap-

\[ VH_k \leftrightarrow VH_{k-1} + H \text{ (at site}_3) \]

✓ Equilibrium between site-1 and site-2
✓ Migration between site-2 and site-3
  ✓ Trap: site-3 to site-2
  ✓ Detrap: site-2 to site-3
✓ Correction of site-3 energy from solution energy

\[ \frac{dc^{VH_k}}{dt} = K_{(k-1)\to k} \times c^{VH_{k-1}} \times c^H_{site_3} + K_{(k+1)\to k} \times c^{VH_{k+1}} \\
- K_{k\to(k-1)} \times c^{VH_k} - K_{k\to(k+1)} \times c^{VH_k} \times c^H_{site_3} \]

**rate equation**

- **trapping**
  \[ K_{(k-1)\to k} = \{N^V_{H_{k-1}} \times p_{trap}^{VH_{k-1}}\} \times \left\{V_{H_{k-1}}^{VH} \times exp\left(-\frac{E^{VH_{k-1}}}{RT}\right)\right\} \]

- **detrapping**
  \[ K_{k\to(k-1)} = \{(k \times f_{VH_{H_k}}^2) \times (N^V_{H_k} \times p_{detrap}^{VH_k})\} \times \left\{V_{H_k}^{VH} \times exp\left(-\frac{E_{detrap}^{VH_k}}{RT}\right)\right\} \]

occupation fraction of each site_2
attempt frequency
energy barrier
2. Derivation of rate equations for V-H interaction in “H in W” validation of the model: VH$_k$ complex fraction at a steady state.

Compare with MD results (2/2)
-- Fraction of V-H complexes in V8-H29 system
2. Derivation of rate equations for V-H interaction in “H in W”

-validation of the model: time evolution of solute H fraction-

Time evolution of solute-H fraction

Time evolution of V-H complexes
Contents

1. Hydrogen diffusivity in W

2. Rate theoretical model for vacancy trap effects on hydrogen diffusivity

3. Experimental studies in SNU
   ✓ Younggil Jin, Nam-Kyun Kim, Jae-Min Song, Ki-baek Roh, Gon-Ho Kim
The ion irradiation condition is relevant to ITER PFC condition: 1st wall ~ $1 \times 10^{21} \text{D}^+ / \text{m}^2 \text{(8-300eV)}$, divertor dome ~ $2 \times 10^{20} \text{D}^+ / \text{m}^2 \text{(33-80eV)}$
Oversaturation Depth Growth Rate (dh/dt)

SIMS depth profile of Deuterium (Qualitative measurement)

Oversaturation depth growth rate

= ion-induced defect generation rate (\( \eta \))

\[
\text{Oversaturation depth growth rate (dh/dt)} = \frac{\text{saturated oversaturation depth}}{\text{time}} = 0.72-1.52 \text{ [pm/s]} \ (16 \text{ nm} \pm 6 \text{ nm/14400 s})
\]

\( \Rightarrow \) This value can be used for determining defect generation rate (\( \eta \)).
1. Olga’s method [2]

- The original model of Olga was designed to describe the effect of ion energy, fluence, and the maximum defect fraction. It’s not the physical model but an empirical form which has high accordance with experiment nevertheless its simplicity.

\[
dW / dt = (1 - f_{bs}) \Psi(x) I_0 \eta (1 - W / W_m)
\]

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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>W(x,t)</td>
<td>defect fraction at time t and position x</td>
</tr>
<tr>
<td>I_0</td>
<td>Effective incident ion flux x area [D/s]</td>
</tr>
<tr>
<td>\eta</td>
<td>defect generation rate</td>
</tr>
<tr>
<td>\Psi</td>
<td>Defect depth distribution factor</td>
</tr>
<tr>
<td>W_m</td>
<td>maximum defect fraction in tungsten</td>
</tr>
<tr>
<td>f_{bs}</td>
<td>backscattering yield of incident D ion</td>
</tr>
</tbody>
</table>

- But the dW/dt is hard to measure directly, thus, Olga arbitrarily take the \( \eta (10^{-3} \) for ion-induced trap [1]) which shows good agreement with experimentally obtained retention data.

Defect fraction estimation: Olga’s model + determined $\eta$ (using dh/dt)

- **Conditions:**
  - **Using defect generation rate ($\eta$):** 0.000786.
  - Incident ion backscattering yield ($f_{bs}$) determined by TRIM with incident ion energy and angle.
  - **Assumption:** Maximum defect fraction in tungsten = 0.05 atomic fraction.
  - Fluence = effective ion flux ($D^+/m^2$-s) x time.

**Defect fraction**

$$W(x,t) = W_m \left(1 - \exp \left(-\left(1 - f_{bs}\right) I_0 \Psi(x) \eta t / W_m \right)\right)$$

<table>
<thead>
<tr>
<th>W(x,t)</th>
<th>defect fraction at time t and position x</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_0$</td>
<td>Effective incident ion flux x area [D/s]</td>
</tr>
<tr>
<td>$\eta$</td>
<td>defect generation rate = 0.78x10^{-3} (expected minimum value)</td>
</tr>
<tr>
<td>$\Psi$</td>
<td>Defect depth distribution factor, 1 in oversaturation depth but 0 for beyond oversaturation depth</td>
</tr>
<tr>
<td>$W_m$</td>
<td>maximum defect fraction in tungsten = 0.05 atomic fraction</td>
</tr>
<tr>
<td>$f_{bs}$</td>
<td>backscattering yield of incident D ion): 50eV $\Rightarrow$ 0.4836, TRIM</td>
</tr>
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</table>

![Defect fraction graph](image)
Determination of Effective Diffusion Coefficient

Effective diffusion coefficient in Olga’s model taken into oversaturation depth

\[ D_{\text{eff}}(x,t) = D_{\text{intrinsic}} \left( 1 - 0.75 \times \exp \left( - (1 - f_{bs}) I_0 \Psi(x) \eta t \right) \right) \]
Simulation of Retention Property for Ion+Neutron Induced Defect in W

Plasma permeation simulation using TMAP4
with Ion-induced defect + Neutron-induced defect Model

<table>
<thead>
<tr>
<th>Plasma exposure condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>D Ion flux, $\Gamma_i$</td>
<td>$5.6 \times 10^{21}$ D$^+$/m$^2$.s</td>
</tr>
<tr>
<td>$f_{\text{backscattering}}$</td>
<td>0.486 (TRIM result)</td>
</tr>
<tr>
<td>Fluence</td>
<td>$\sim 4.0 \times 10^{25}$ D/m$^2$</td>
</tr>
<tr>
<td>Effective ion flux</td>
<td>$2.72 \times 10^{21}$ D$^+$/m$^2$.s</td>
</tr>
<tr>
<td>Impact energy, $E_i$</td>
<td>50 eV/D$^+$</td>
</tr>
<tr>
<td>Ion implanting depth</td>
<td>1.5 nm</td>
</tr>
<tr>
<td>$W_{m,\text{intrinsic}}$</td>
<td>0.0004 (const.)</td>
</tr>
<tr>
<td>$W_{m,\text{ion-induced}}$</td>
<td>0.05 (function of time)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Defect parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intrinsic defect faction, $W_{\text{intrinsic}}$</td>
<td>0.0004 (dislocation, uniform in volume.)</td>
</tr>
<tr>
<td>Ion-induced defect faction, $W_{\text{ion-induced}}$</td>
<td>$W(x,t) = W_m \left(1 - \exp \left(-1 - f_{bs}I_0\Psi \times \eta \right) / W_m \right)$</td>
</tr>
<tr>
<td>Defect growth rate, $\eta$</td>
<td>$0.78 \times 10^{-3}$</td>
</tr>
<tr>
<td>Effective diffusion coefficient, $D$</td>
<td>$D_{eff}(x,t) = D_T \left(1 - 0.75*\exp \left(-1 - f_{bs}I_0\Psi \times \eta \right) / u_m \right)$</td>
</tr>
<tr>
<td>Trapping rate</td>
<td>$K_I = 2.92 \times 10^{12} \exp \left(-0.39 eV / kT \right)$</td>
</tr>
<tr>
<td>De-trapping rate</td>
<td>$K_{I,\text{intrinsic}} = 8.4 \times 10^{12} \exp \left(-0.85 eV / kT \right)$ $K_{I,\text{ion-induced}} = 8.4 \times 10^{12} \exp \left(-1.43 eV / kT \right)$</td>
</tr>
</tbody>
</table>
Retrieval Scaling Law for Ion-induced W

Broad Empirical Scaling laws
(Tanabe, 2014 [4])

Scaling laws
(based on ion induced defect considered TMAP4 results)

Scaling law: retention = a*fluence^b

- Parameters in scaling law (a ~10^3-10^6, b=0.6-0.8) are a function of ion flux (Γ_i), ion energy (E_i) and PFC temperature (T) and ion-induced defect generation rate (η).
- The new scaling law narrow down the Tanabe’s scaling law (b=0.3-1.0): reduce uncertainty in expectation.

Scaling law for ion-induced defect only

scaling law: retention = \( a \cdot \text{fluence}^b \)

\[
a \sim 10^3 - 10^6, \quad b = 0.6 - 0.8
\]

- The higher slope ‘a’ and The lower exponent ‘b’ (0.4-0.5 < 0.6-0.8)
  resulted from ion-induced defect trapping energy (\( E_b \) for ion = 1.45 eV, 
  \( E_b \) for n = 1.85 eV) and spatial distribution (ion ~ 16 nm, n ~ entire bulk)
Summary

1. Hydrogen diffusivity in W

(Frauenfelder) \( D = 4.1 \times 10^{-7} \exp(-0.39 \, e \, V / k \, T) \)

(Heinola; high-T data fitting) \( D = 1.58 \times 10^{-7} \exp(-0.25 \, e \, V / k \, T) \)

2. Rate theoretical model for vacancy trap effects on hydrogen diffusivity
   ✓ The rate constants are established using transition state theory.
   ✓ [Plan] We will apply this method to determine trap/detrap rate constants for V-H interactions in W using DFT.

3. Experimental studies in SNU
   ✓ How should we consider effective diffusivity in TMAP.