He Retention in Tritides: Importance of Bubble Location and Spacing Distribution

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H and He in Materials Workshop, Albuquerque, Feb 6-7, 2007

• Helium Bubble Linkage and the Transition to Rapid He Release in Pd Tritide
  (SAND 2006-7779)

• Effects of the Beta-Induced Reactivity of Er Tritide: Simulation Experiments
The Bubble Evolution Model

Imposed Conditions: Material, Geometry, Environment

Mechanism Detail

- Self-trapping Energies
- He Mobilities
- Mech. Props
- PCT(x,t)
- Material Props.
- First Principles
- DFT
- Mechanism Detail & Discovery
- Atomistic Comp.
- MD Simulations

Continuum Model

- Bubble Nucleation
  by He Atom Self-Trapping
  (with Trapping at Defects)
- Bubble Growth
  by Dislocation Loop Punching
  (with Bubble Interactions)
- Bubble Linkage
  by Inter-Bubble Ligament
  Fracture
- Network Generation
  Percolation of linked-bubbles

Experiments

- He Implant/Re-emission
- He Rel. & ERF
- SEM & TEM
- \(^3\)He NMR (\(\Delta T, \Delta \Phi\))
- Swelling & \(\Delta S/\Delta T\)
- PCT Shifts
- XRD (\(\Delta a/a\))
- TDS
  (both implanted & aged material)

Fractional He Release (time, Temp...)
Model predicts bubble characteristics and He the release spectrum.

Computed He release shows all the features observed for tritides.

Initial drop
Low early release fraction
Slow rise with age
Onset of accelerated release

He release spectrum is critically dependent on the bubble spacing distribution.
The bubble spacing distribution in PdTx was determined by $^3$He NMR.

- $^3$He $T_1$ (motion) separates sol-He from liq-He in bubbles.
- Growth relations convert fluid fractions to bubble distributions.

The constant spacing distribution - verifies nucleation has stopped - provides a sensitive test of the nucleation and growth models.
The Critical He/M for Bubble Linkage depends on bubble spacing.

- Stress created by neighbors leads toward bubble coalescence.
- Stress-directed bubble growth occurs only for non-symmetric arrays.
  - requires a spacing distribution.

- SD-growth is interrupted by inter-bubble ligament fracture.
  - linkage starts with closely-spaced bubbles.
Linked Volume Fraction increases with He/M concentration

- Linkage by SD-growth to IB-fracture
  - begins at .32 He/M
  - at .44He/M, incorporates widely-spaced bubbles
  - at .39 He/M, reaches the Critical Volume Fraction for infinite percolation:

- From classical percolation theory in 3d, $V_C = .15$

- In “rapid release”, the release rate is 1-2 times the generation rate:
  \[
  \text{Rel/Gen} = (\text{He/M}) \frac{dV}{d(\text{He/M})} \approx .4(3) = 1.2
  \]
Percolation of surface-connected, linked-bubble clusters gives the *transition* to rapid release.

- Fractional He release:
  - spherical particles
    \[ V_P = V [1-(1-d_C/R_P)^3] \]
  - films (thickness L) on substrates
    \[ V_F = V (d_C/L) \]

- Linked cluster diameter,
  \[ d_C (\text{nm}) = 1.67/(V_C-V)^{0.675} \]

- Linkage percolation is sensitive to details of the bubble spacing distribution.
Early He release depends on the bubble density and defect trapping near surfaces.

- Bubble denuded zone $d_Z$ produced by He self trapping: 50-100 Å

\[
dc_2/dt = ps_1c_m^2 - q_2c_2 - ps_2c_mc_2
\]

- The mobile Helium concentration near the surface is too low to nucleate bubbles.

- The He escape length $\lambda_{esc} \approx d_Z/2$ produces an early release fraction.
  - For PdT, $\lambda_{esc} \approx 40\text{Å}$
However, for Er tritide films, only $^3$He born within the *top monolayer* escapes!

- He escape depth from [111] oriented ErT$_2$ films = 1.8 Å (Snow et al, 2006)

- What makes He immobile in this layer?
  1) Trapping at Er$_2$O$_3$ precipitates?
     - requires O/Er ~1 in “hydride”
  2) Trapping within Er(OT)$_3$ layer?
  3) Er(H,T)$_3$ near-surface layer?
     - produced by H$_2$O oxidation
     - He migration blocked by H

- Testing (3) using ErH$_2$ films, exposed to water vapor in the ALS (LBNL).
  - radiation-enhanced oxidation
  - H-pickup (resistivity, TDS)
  - effect on He migration (HeIRE)
  - work in progress
Energy deposition by synchrotron-based X-rays is similar to tritium betas.

Comparison of Energy Deposition Spectra
Tritium=blues, X-rays=reds (LEX-D code)

- Same average energy of 5-10 keV.
  - Power deposited by tritium betas is $E \times N(E)$

- Energy is deposited uniformly throughout the film
  - Only 10% of incident energy is absorbed,
X-ray exposures of ErH$_2$ films were done at the Advanced Light Source synchrotron (LBNL)

- Experimental Arrangement:

- Environment: Water vapor in flowing He.
  - Eliminated ozone produced by X-rays in air.
We exposed a stripe across the samples.

#108K
1.3 hr
.17 Torr, 0.8% RH
120 ma-hr

#170K
1.5 hr
10 Torr, 48% RH
120 ma-hr

#168K
7.5 hr
9.5 Torr, 45% RH
680 ma-hr
X-ray exposures in $\text{H}_2\text{O}$ vapor increased the oxide thickness, similar to betas.

- Nascent-H pickup is expected to be too small to discern by thermodesorption.

- Plans (delayed by funding):
  - Use $\text{D}_2\text{O}$
  - Expose larger ErH$_2$ area
  - Quantify nascent-D by NRA or TDS
Hydrogen pickup can be deduced *in-situ* from the change in electrical resistivity of the film.

- 4-point resistance probe uses films on quartz discs.

**Hydriding with H\textsubscript{2}O**

![Graph showing modeled behavior with and without oxide growth](image)

- Modeled Behavior
  - 2H added per O
- With film thinning by oxide growth
- No thinning

*Note: The graph illustrates the change in normalized resistance versus H/Er ratio, showing distinct phases labeled α, α + β, β, and β + γ.*
Near-surface He diffusion and trapping parameters are measured by Implant/Re-emission.

- The HeIRE technique uses small volumes & rapid valve timing.

- He re-emission is fit to diffusive release with self-trapping.

> Measured diffusivity in Pd agrees with model value for average bubble density.
Experiments with ErH$_2$ films show lower diffusivity and significant He trapping at RT.

- He diffusion through Er$_2$O$_3$ is assumed rapid.
- Early time dependence is approximated by draining of slab ($L=$He$^+$ range, SRIM):
  \[ p(\text{He}) \approx \frac{4Dt}{\pi L^2} \]
- The re-emission fraction indicates lots of low-energy traps:

<table>
<thead>
<tr>
<th>$T(\degree C)$</th>
<th>release/implant</th>
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</thead>
<tbody>
<tr>
<td>27</td>
<td>.018</td>
</tr>
<tr>
<td>100</td>
<td>.06</td>
</tr>
<tr>
<td>150</td>
<td>.17</td>
</tr>
<tr>
<td>200</td>
<td>.38</td>
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5 keV, 10 $\mu$C pulse
The cause of low early He release from Er tritide films remains a mystery.

• Films appear to possess a “hydride phase” layer with significant He trapping.

Er films have an Er(OH)\(_3\) layer over Er\(_2\)O\(_3\).
(Y.G. Wu et al., Proc. SPIE 4086 (2000) 360 & observed by Roland Schulze, LANL)

Tritide betas appear to assist
- migration of OH through oxide
- conversion of Er(OH)\(_3\) to Er\(_2\)O\(_3\)?
  \[ \text{Er}(\text{OH})_3 \rightleftharpoons 326.8 \text{ kcal/mole} \]
  \[ \text{Er}_2\text{O}_3 \rightleftharpoons 453.6 \text{ kcal/mole} \]

Reaction of OH with ErH\(_2\) beneath the oxide should produce more Er\(_2\)O\(_3\) & stable ErH\(_3\):
  \[ 9 \text{Er}T_2 + 3 \text{OH} = \text{Er}_2\text{O}_3 + 7 \text{Er}(H,T)_3 \]

• The beta-enhanced surface chemistry of tritides can be simulated using synchrotron X-rays on hydrides. -- We have observed oxide growth.

• Effects on He migration can be examined by implant/re-emission techniques.