D loss as a function of temperature in ErD$_2$ films on kovar with and without an intermediate Mo diffusion barrier

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Introduction

- SNL uses Er as an occluder material
- Both Mo and kovar, an Fe, Ni, Co alloy are used for substrates
- The storage capacity of the kovar/Er occluder stack is significantly lower than that of the Mo/Er occluder stack
Kovar substrate suspected

- Mixing from some thermal process steps thought to drive H,D,T loss
  - This does not appear to be a problem with the Mo/Er occluder stacks

- Diffusion barriers investigated to prevent mixing
Mo was chosen as a diffusion barrier*

- Auger Depth Profiles after 564 °C 2 hr. anneal
  - Unknown phases in XRD pattern, \( \text{Er}_2\text{O}_3 \) present as well
  - Auger data showed evidence of mixing
  - Oxygen peak near Er/Kovar interface suggests possible oxide layer
  - G:M was 0.703 on similar specimen

- XRD showed some \( \text{Er}_2\text{O}_3 \)
  - Auger data showed O peak at Er/Mo interface
  - G:M was 1.827 on similar specimen

* SAND2006-5864
Motivations for IBA Work

• Determine mechanism(s) for D loss

• Determine when diffusion barrier fails

• Compare effectiveness of two Mo diffusion barriers
  – Sputtered Mo
  – Evaporated Mo
Outline of IBA Experiments

- **Substrates**
  - ¾” diameter kovar coupons
  - Clean and Degrease
  - Wet H₂ Fire and Vac Fire

- **Film Deposition**
  - Mo – 2 kÅ sputtered at ambient Temp
  - Mo – 2 kÅ ebeam evap at 450 °C
  - Er Evaporated at ambient & 450°C

- **Loading**
  - Coupons D₂ loaded in PCT using nominal conditions

- **Characterization**
  - RBS
  - NRA
• Metals (Er, Mo, Kovar) are analyzed by Rutherford backscattering with 2 MeV $^4$He.
• The energy spectrum of elastically scattered $^4$He is measured.
• $^4$He scattered from lighter elements and from greater depths reaches the detector with less energy.
• The energy scale is transformed to a depth scale using known stopping power.
• Yield is transformed to concentration using known scattering cross sections.
• Mixing at interfaces broadens the edges.
The concentration of deuterium (D) versus depth was measured by $D(^{3}\text{He},p)\alpha$ nuclear reaction analysis.

- An analysis beam of 0.8 MeV $^{3}\text{He}$ is directed onto the target.
- $^{3}\text{He}$ reacts with D in the tile producing protons with $E \sim 12$ MeV.
- The energy spectrum of the protons is measured by an annular detector.
- More numerous but lower energy elastically scattered $^{3}\text{He}$ are stopped by a range foil.
- Protons from greater depths reach the detector with higher energy.
- The energy scale is transformed to a depth scale using known stopping power.
- Yield is transformed to concentration using known reaction cross section.
Time/Temperature Schedule of In situ Anneals

- **Isothermal Anneals**
  - Ramp up ~ 104°C/min
  - 20 min
  - Ramp down Natural rate
  - T_IBA < 80°C
  - Time 20 min
  - Ramp up ~ 104°C/min
  - T_IBA < 80°C
  - Time 40 min
  - Ramp down Natural rate

- **Isochronal Anneals**
  - Ramp up ~ 104°C/min
  - 20 min
  - Ramp down Natural rate
  - T_IBA < 80°C
  - Time 20 min
  - Ramp up ~ 104°C/min
  - T_IBA < 80°C
  - Time 40 min
  - Ramp down Natural rate
## Sample Process & Characterization Summary

<table>
<thead>
<tr>
<th>Sample ID number</th>
<th>Mo deposition method (temperature)</th>
<th>E-beam Er deposition temperature</th>
<th>Sample Hydrided with D₂?</th>
<th>Characterization summary</th>
</tr>
</thead>
<tbody>
<tr>
<td>012</td>
<td>No Mo</td>
<td>450 °C</td>
<td>No</td>
<td>20 min Isochronal (200-600 °C) RBS</td>
</tr>
<tr>
<td>007</td>
<td>No Mo</td>
<td>Ambient</td>
<td>No</td>
<td>Isothermal RBS at 450°C</td>
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<tr>
<td>009</td>
<td>No Mo</td>
<td>450 °C</td>
<td>Yes</td>
<td>20 min Isochronal (200-600 °C) RBS</td>
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<tr>
<td>010</td>
<td>No Mo</td>
<td>450 °C</td>
<td>Yes</td>
<td>Isothermal (500 °C) RBS &amp; NRA</td>
</tr>
<tr>
<td>011</td>
<td>No Mo</td>
<td>450 °C</td>
<td>Yes</td>
<td>Isothermal (550 °C) RBS &amp; NRA</td>
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<tr>
<td>014</td>
<td>Sputtered Mo (ambient)</td>
<td>450 °C</td>
<td>Yes</td>
<td>20 min Isochronal (200-600 °C) RBS &amp; NRA</td>
</tr>
<tr>
<td>017</td>
<td>E-beam Mo (450 °C)</td>
<td>450 °C</td>
<td>Yes</td>
<td>20 min Isochronal (200-600 °C) RBS &amp; NRA</td>
</tr>
</tbody>
</table>
Isochronal anneals of Er/kovar

Isochronal anneals (20 min) 200 - 600°C of sample 012: 5 kÅ Er (450°C)/kovar

Change evident between 400-450 °C
Isochronal anneals of ErD$_2$/kovar

- RBS & NRA data collected after Isochronal (20 min) anneals of Er deposited on kovar at 450°C and D$_2$ loaded (009)

- Changes begin between 450-500°C and become rapid above 500°C.
- NRA spectra show D loss is from ErD$_2$/kovar interface
- D loss driven by mixing between kovar and ErD$_2$
500 °C Anneals of ErD₂/kovar

- RBS & NRA data collected after Isothermal (500 °C) anneals of Er deposited on kovar at 450°C and D₂ loaded (010)

- Mixing is evident between 35 & 75 min.
- D loss predominantly from ErD₂/kovar interface
- D loss driven by mixing between kovar and ErD₂
550 °C Anneals of ErD$_2$/kovar

- RBS & NRA data collected after **Isothermal** (550 °C) anneals of Er deposited on kovar at 450°C and D$_2$ loaded (011)

- Mixing is evident after only 5 min.
- D loss predominantly from ErD$_2$/kovar interface
- D loss driven by mixing between kovar and ErD$_2$
Mixing of Er and kovar

\[ \sqrt{(Dt)} \sim \Gamma \]

\[ \Gamma \text{(nm)} = (16 \ln(2) \cdot D \cdot t)^{1/2} \]

- \( D = D_0 \exp\left(-\frac{E_a}{kT}\right) \)
- \( E_a = 2.1 \text{ eV} \)
- \( D_0 = 0.071 \text{ cm}^2/\text{s} \)

\[ y = 0.4562x \quad R^2 = 0.9429 \]

\[ y = 1.1756x \quad R^2 = 0.9734 \]

- We’re assuming Er is moving through a “static” matrix when in reality it’s constantly changing
Isochronal anneals with sputtered Mo barrier

- RBS & NRA data collected after isochronal (20 min) anneals of sample (014) 5 kÅ Er (450°C dep)/2 kÅ Mo (sputtered at ambient T)/kovar with nominal D₂ loading

- Diffusion through Mo begins between 500-550°C
- D loss begins between 500-550°C but is more uniform throughout film
- D loss is driven by thermal decomposition of ErD₂
Isochronal anneals with e-beam Mo barrier

- RBS & NRA data collected after **Isochronal** (20 min) anneals of sample (017) 5 kÅ Er (450°C dep)/2 kÅ Mo (**e-beam 450 °C**) / kovar with nominal D₂ loading

- Diffusion through Mo begins above 550°C
- D loss begins between 500-550°C and is uniform throughout film
- D loss is driven by thermal decomposition of ErD₂
Microstructure differences in Mo films observed during scoping study*

- TEM EDS Luke Brewer 1822

  - Sample ID 23: kovar / 2 kÅ Mo (e-beam evap) / ErHD annealed at 564 °C for 2 hrs. in vacuum (~10⁻⁸ torr)

  - Sample ID 42: kovar / 2 kÅ Mo (sputter) / ErHD annealed at 564 °C for 2 hrs. in vacuum (~10⁻⁸ torr)

- Sputtered Mo shows evidence of Er diffusion along grain boundaries of columnar grains

*SAND2006-5864
Conclusions

• Substantial mixing occurs at 450°C for Er/Kovar and 500 °C for ErD₂/kovar

• Two mechanisms for D loss
  – Mixing with Substrate (< 500 °C)
    • Diffusion barrier may address this
  – Thermal Decomposition (> 500 °C)
    • Understanding of kinetics of loading/unloading needed to address this

• 500 & 550°C data sets from ErD₂/kovar yield information about mixing
  – Diffusion model of Er with \( E_a = 2.1 \) eV and \( D_0 = 0.071 \) cm²/s
  – Assumes Er is moving through a "static" matrix when matrix is actually changing

• Mo can act as diffusion barrier
  – ErD₂/kovar mixing evident at 500 °C
  – ErD₂/Mo(sputtering)/kovar mixing evident between 500-550 °C
  – ErD₂/Mo(e-beam evap)/kovar mixing evident between 550°C-600°C
  – Microstructure differences between Mo films may explain why the e-beam evap Mo film is a better diffusion barrier than the sputtered Mo film
Acknowledgments

• IBA Studies

• Scoping Study

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Isochronal and Isothermal anneals of Er/kovar

- Isochronal anneals (20 min) 200 - 600°C of sample 012: 5 kÅ Er (450°C)/kovar
- Isothermal anneals at 450°C of sample (007): 5 kÅ Er(ambient)/kovar

- Change evident between 400-450 °C
- Ambient Er shows mixing from both front at back at 450°C
  - O₂ or H₂O reaction from Er surface moving into film?