SAND2008-0575C

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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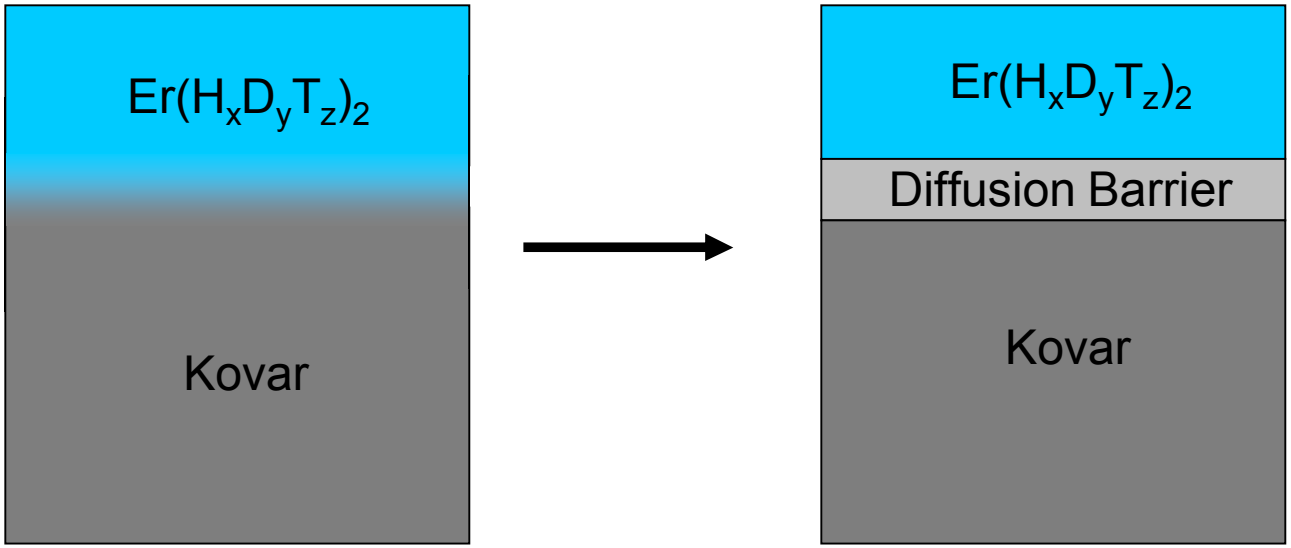
Introduction

- SNL uses Er as an occluder material for hydrogen isotopes in neutron generators
- 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**

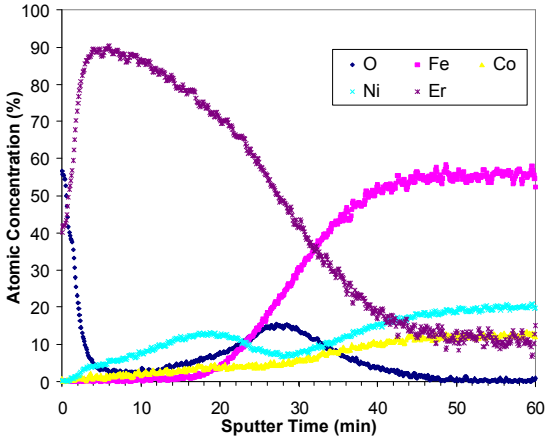
- **Diffusion barriers investigated to prevent mixing**

Mo was chosen as a diffusion barrier*

ErD_2 5 kÅ
kovar

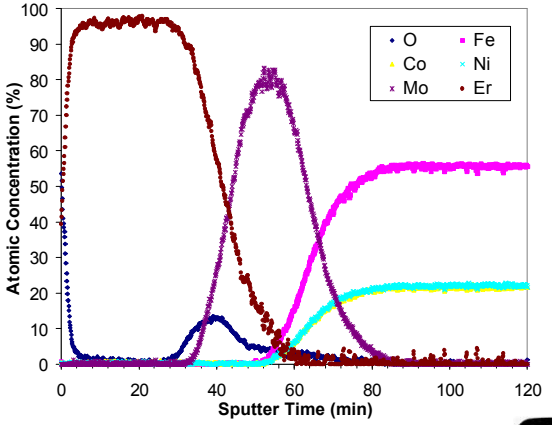
- Unknown phases in XRD pattern, Er_2O_3 present as well
- Auger data showed evidence of mixing
- Oxygen peak near Er/Kovar interface suggests possible oxide layer
- G:M was 0.703 on similar specimen

- Auger Depth Profiles after 564 °C 2 hr. anneal



ErD_2 5 kÅ
Mo (e-beam) 2 kÅ
kovar

- XRD showed some Er_2O_3
- Auger data showed O peak at Er/Mo interface
- G:M was 1.827 on similar specimen



*SAND2006-5864

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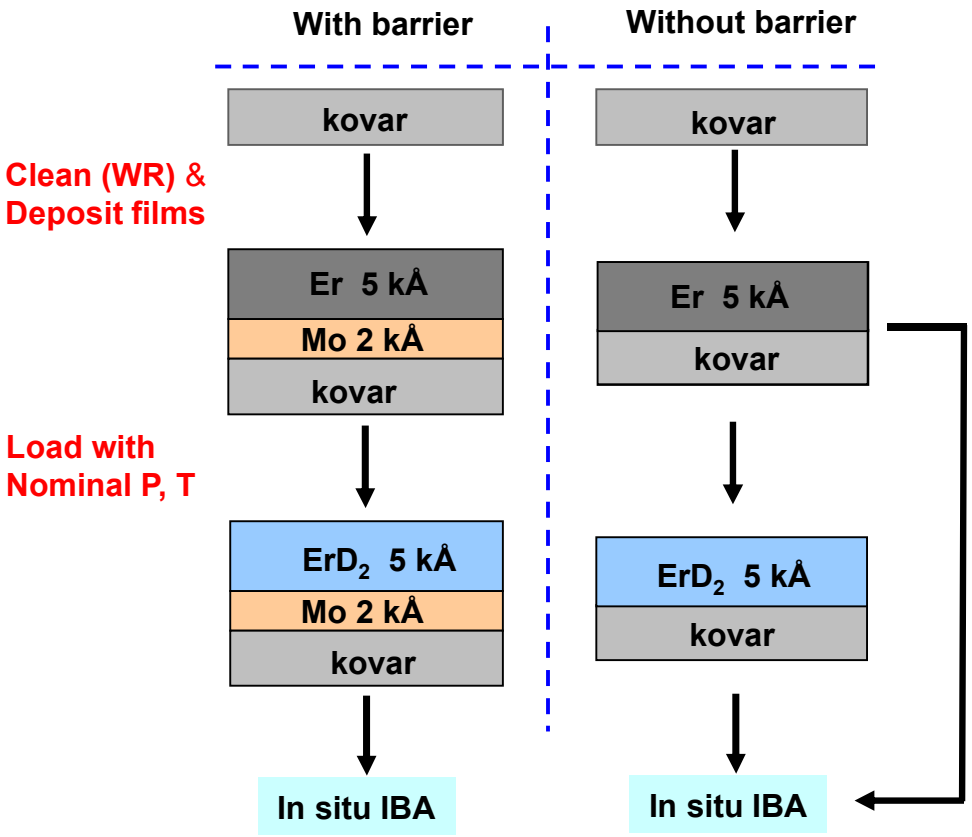
Motivations for IBA Work

- 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 H_2 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 D_2 loaded in PCT using nominal conditions
- Characterization
  - RBS
  - NRA



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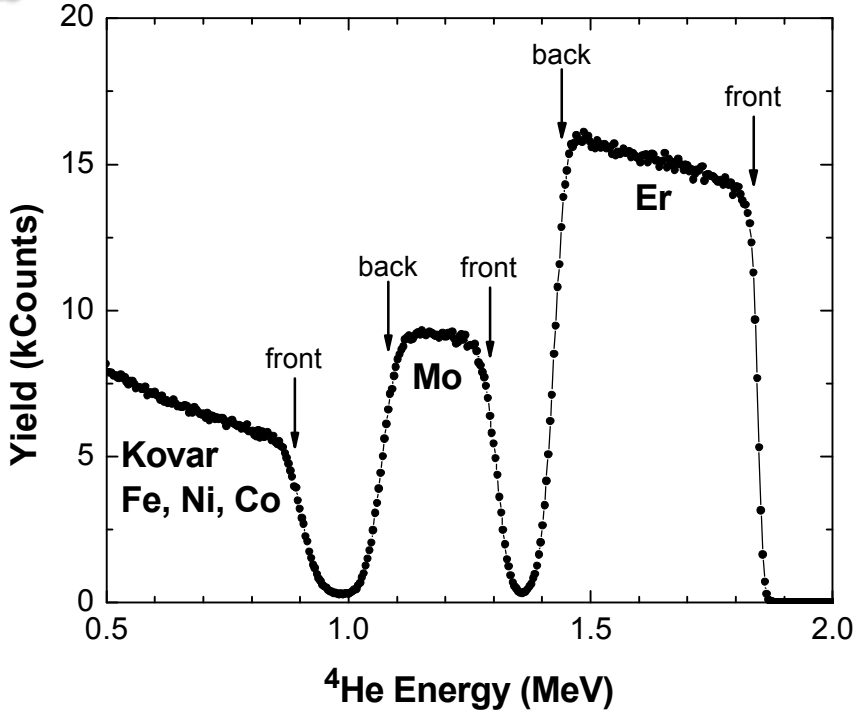
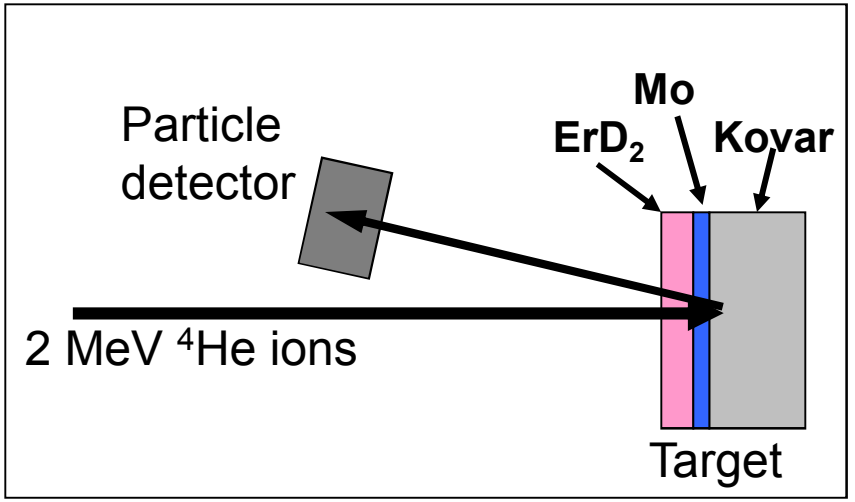
Rutherford Backscattering (RBS)





- 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.

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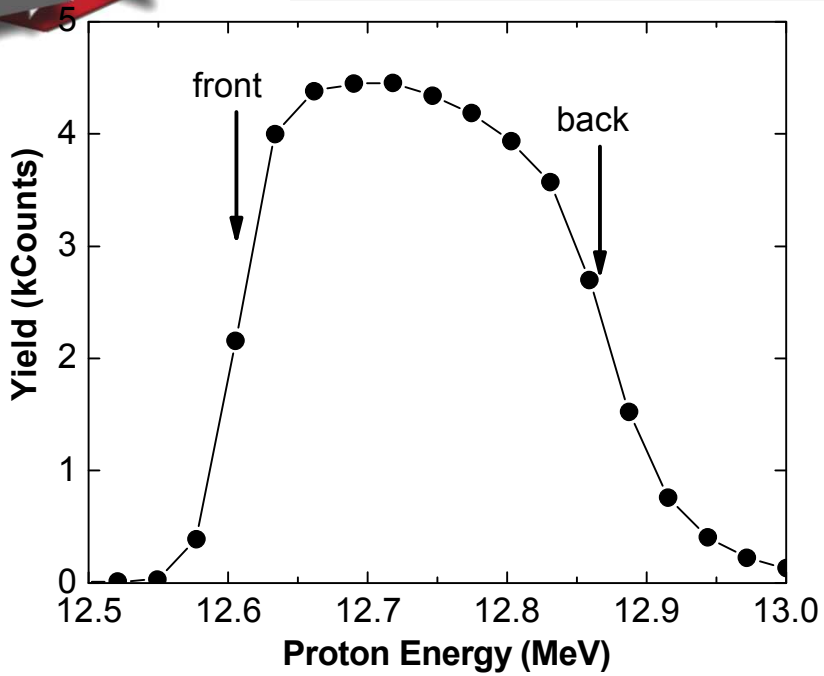
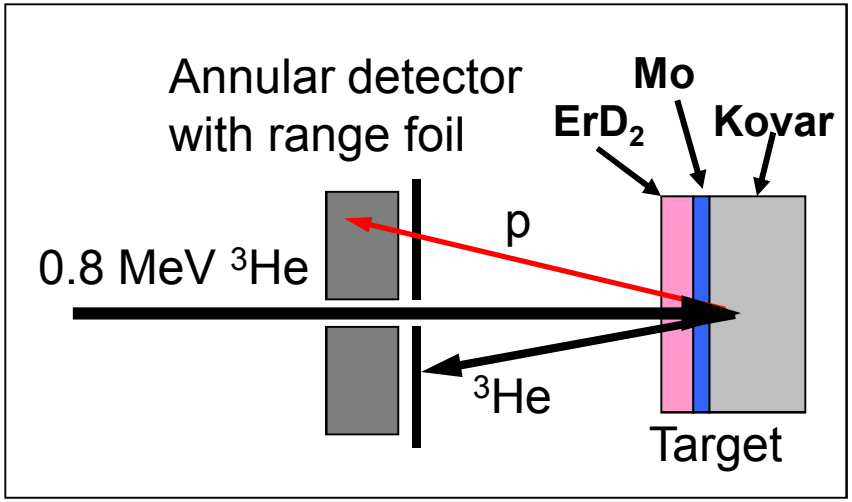
Nuclear Reaction Analysis (NRA)





- The concentration of deuterium (D) versus depth was measured by D(^{3}He,p)α nuclear reaction analysis.
- An analysis beam of 0.8 MeV ^{3}He is directed onto the target.
- ^{3}He reacts with D in the tile producing protons with E ~ 12 MeV.
- The energy spectrum of the protons is measured by an annular detector.
- More numerous but lower energy elastically scattered ^{3}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.

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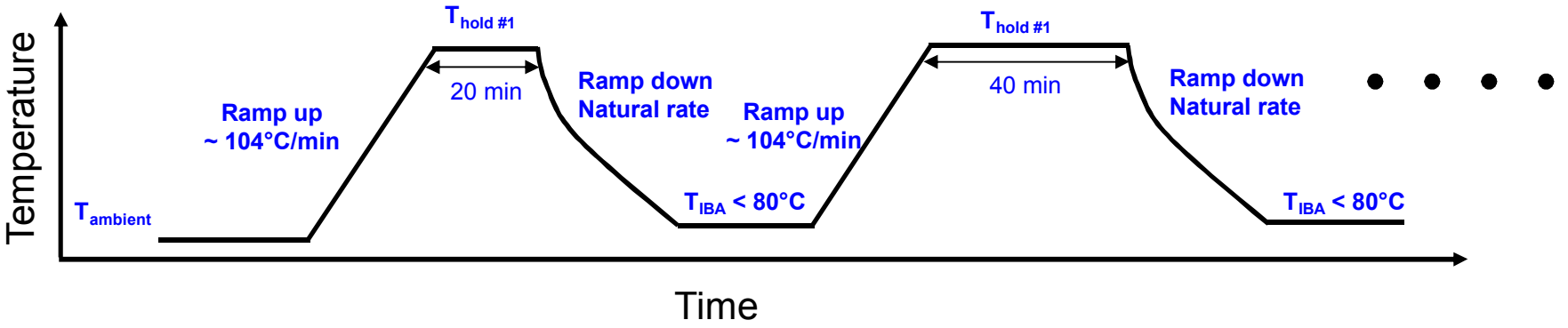
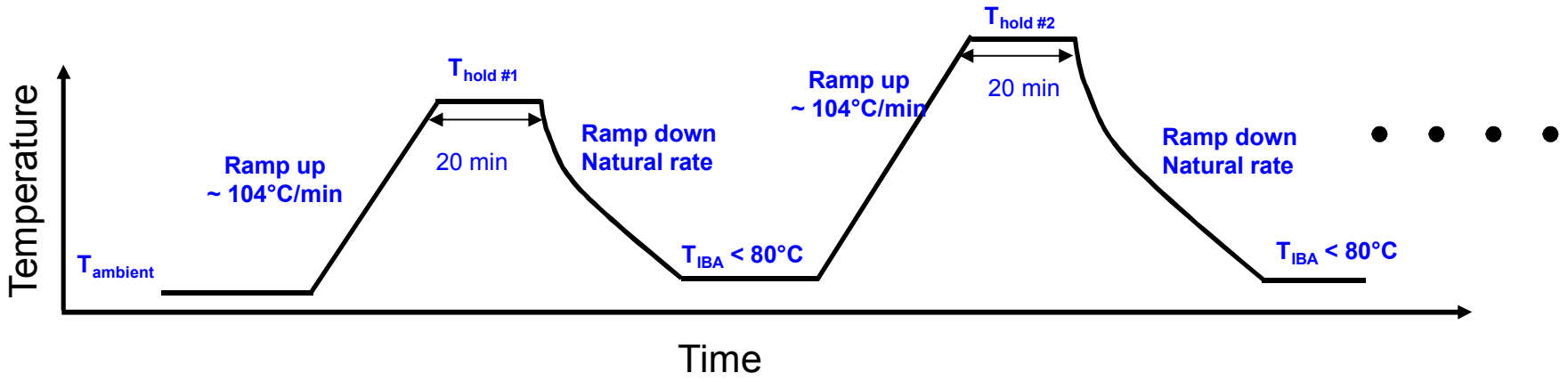
Time/Temperature Schedule of In situ Anneals

- Isothermal Anneals



- Isochronal Anneals



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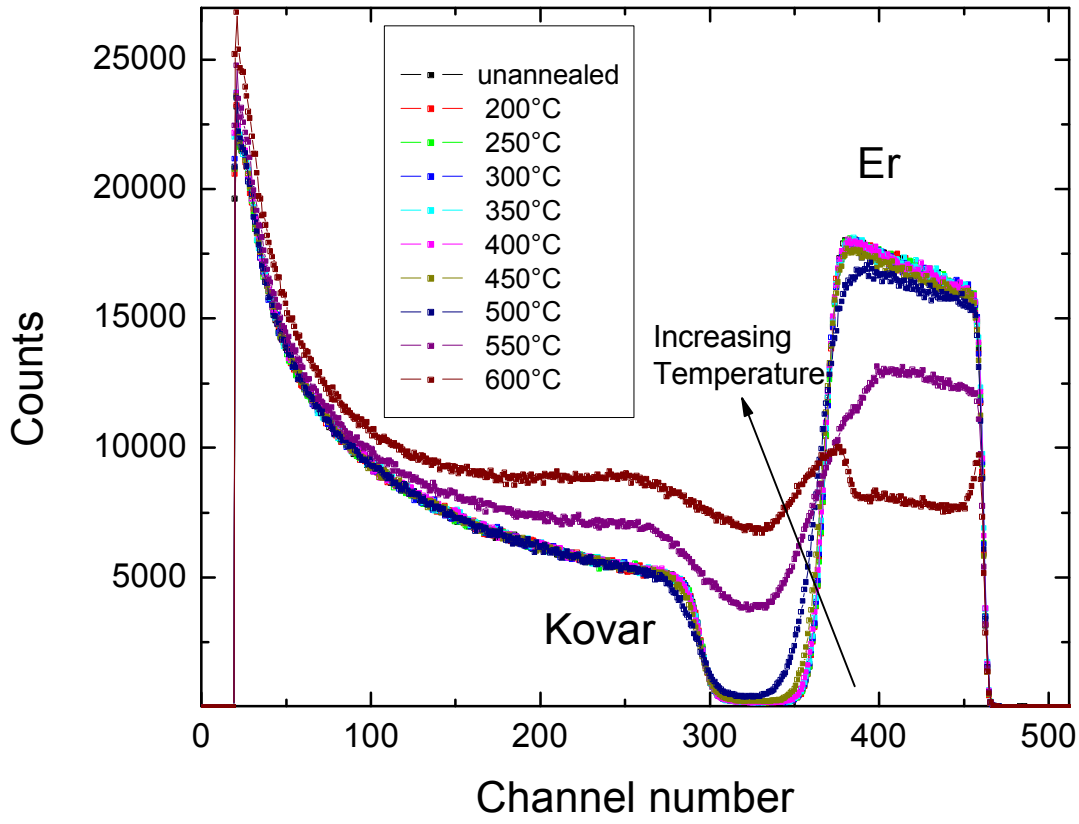
Sample Process & Characterization Summary

Sample ID number	Mo deposition method (temperature)	E-beam Er deposition temperature	Sample Hydrided with D_2 ?	Characterization summary
012	No Mo	450 °C	No	20 min Isochronal (200-600 °C) RBS
007	No Mo	Ambient	No	Isothermal RBS at 450°C
009	No Mo	450 °C	Yes	20 min Isochronal (200-600 °C) RBS
010	No Mo	450 °C	Yes	Isothermal (500 °C) RBS & NRA
011	No Mo	450 °C	Yes	Isothermal (550 °C) RBS & NRA
014	Sputtered Mo (ambient)	450 °C	Yes	20 min Isochronal (200-600 °C) RBS & NRA
017	E-beam Mo (450 °C)	450 °C	Yes	20 min Isochronal (200-600 °C) RBS & NRA

Isochronal anneals of Er/kovar

Er 5 kÅ Ambient & 450 °C
kovar

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



- Change evident between 400-450 °C

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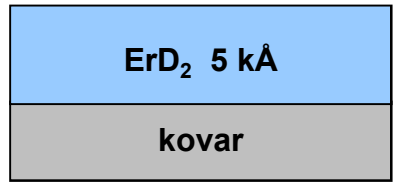
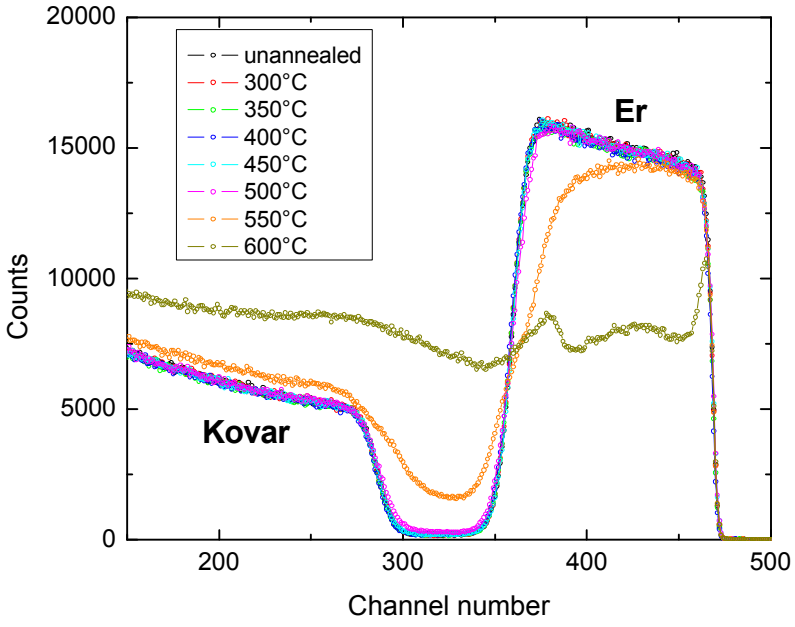
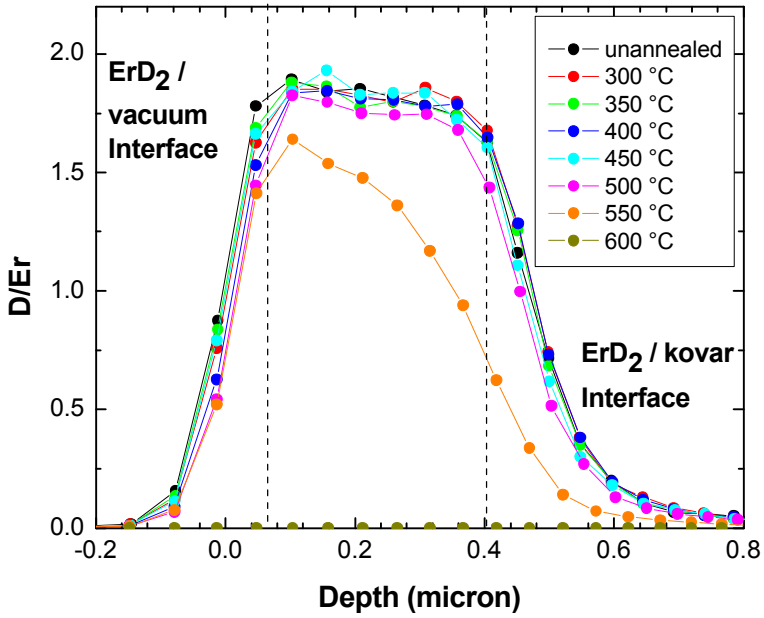
Isochronal anneals of ErD_2/kovar



- 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

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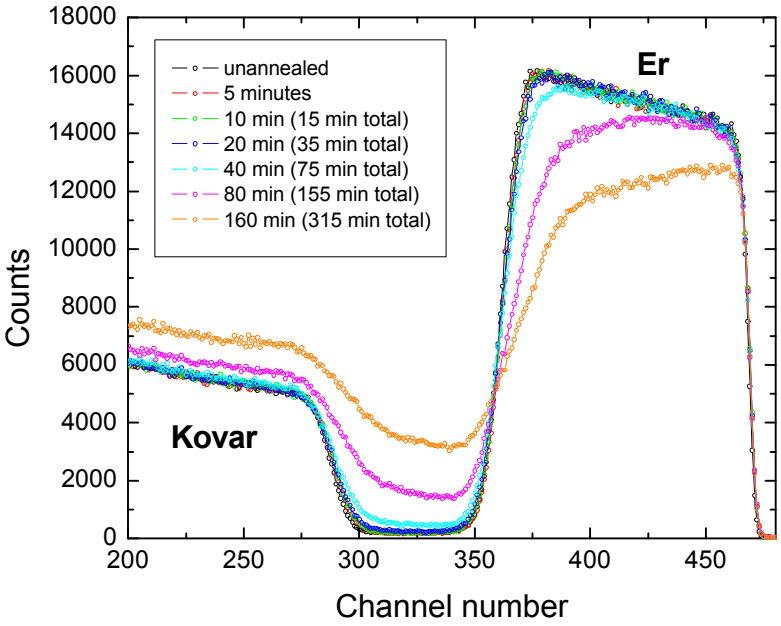
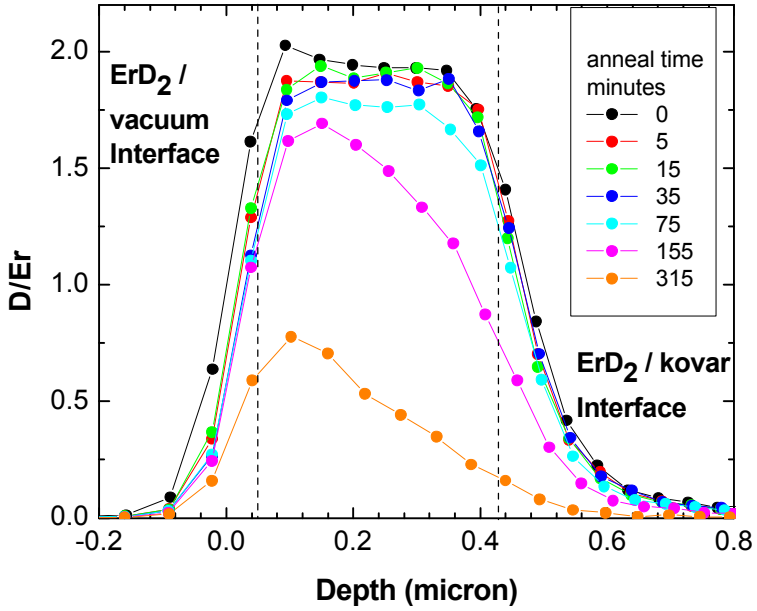
500 °C Anneals of ErD_2/kovar

ErD_2 5 kÅ
kovar

- RBS & NRA data collected after Isothermal (500 °C) anneals of Er deposited on kovar at 450°C and D_2 loaded (010)





- Mixing is evident between 35 & 75 min.
- D loss predominantly from ErD_2/kovar interface
- D loss driven by mixing between kovar and ErD_2

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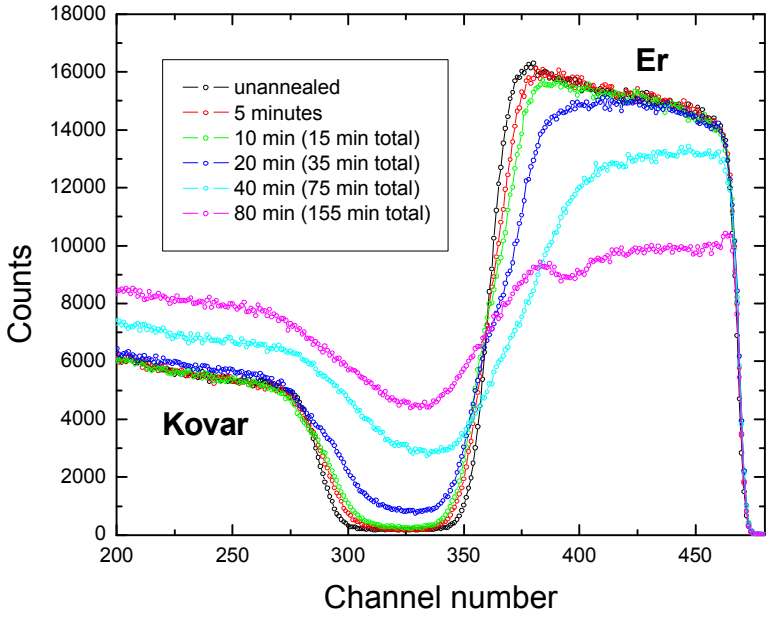
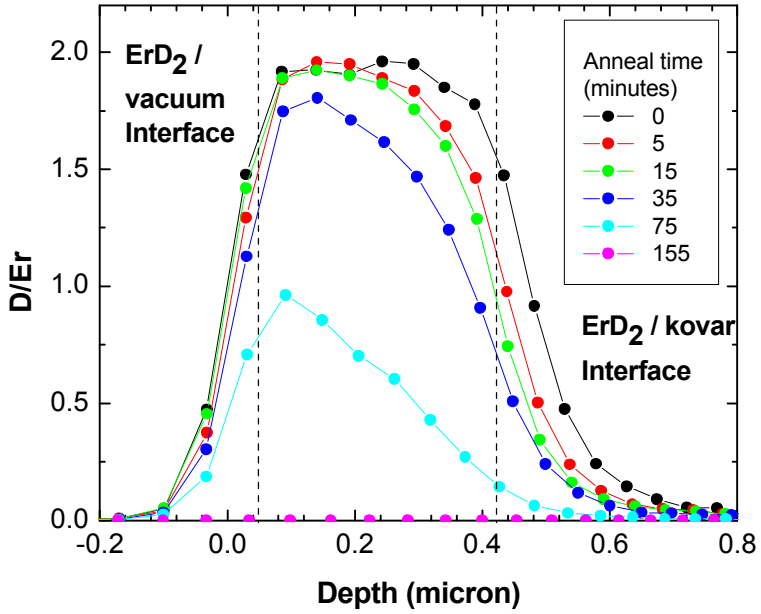
550 °C Anneals of ErD_2/kovar

ErD_2 5 kÅ
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

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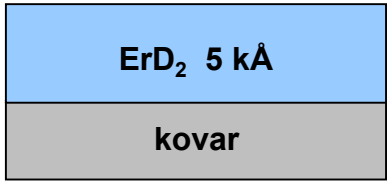
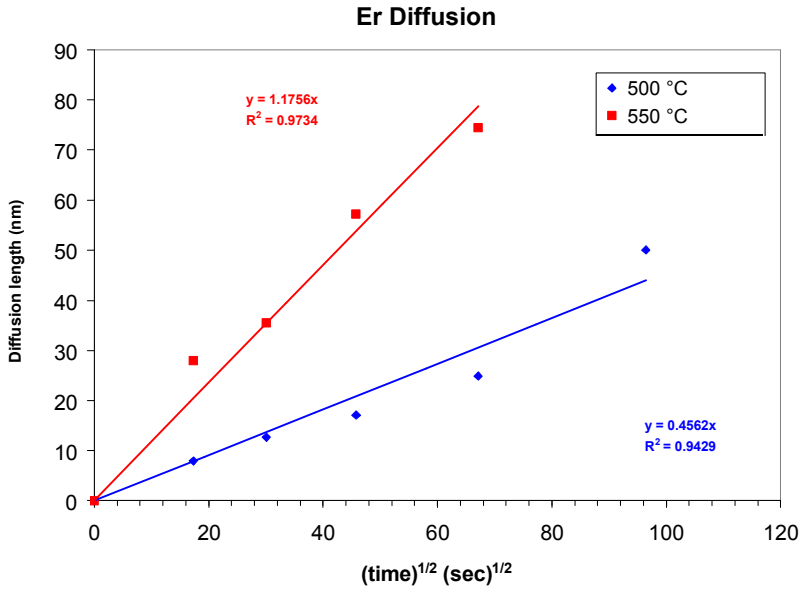
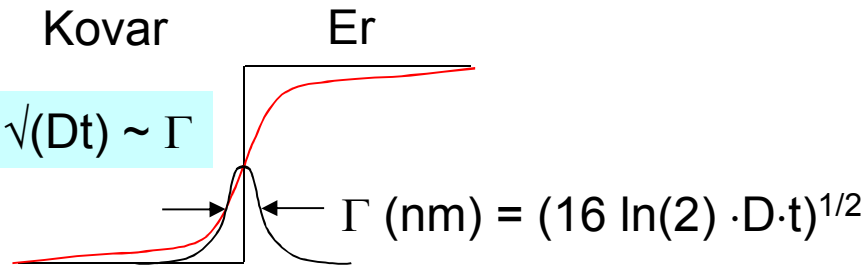
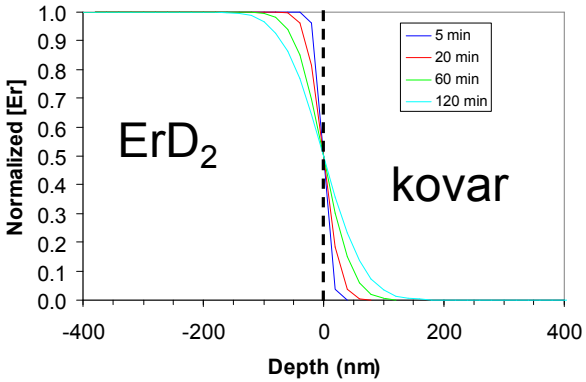
Mixing of Er and kovar

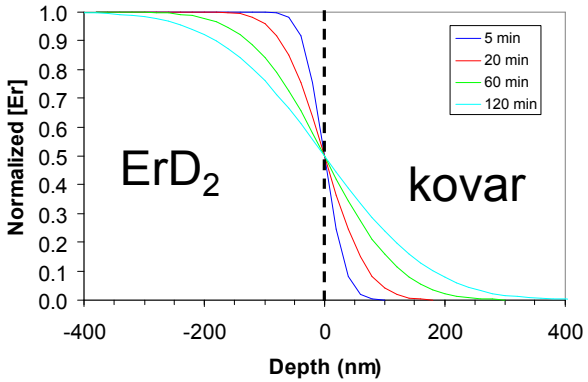






- $D = D_0 Exp(-E_a/kT)$
- E_a = 2.1 eV
- D_0=0.071 cm^2/s





- We're assuming Er is moving through a "static" matrix when in reality it's constantly changing

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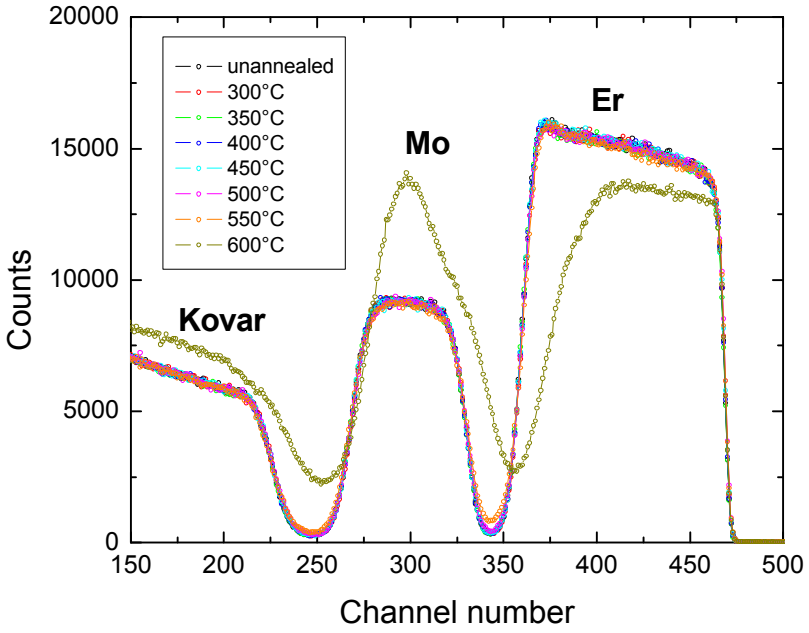
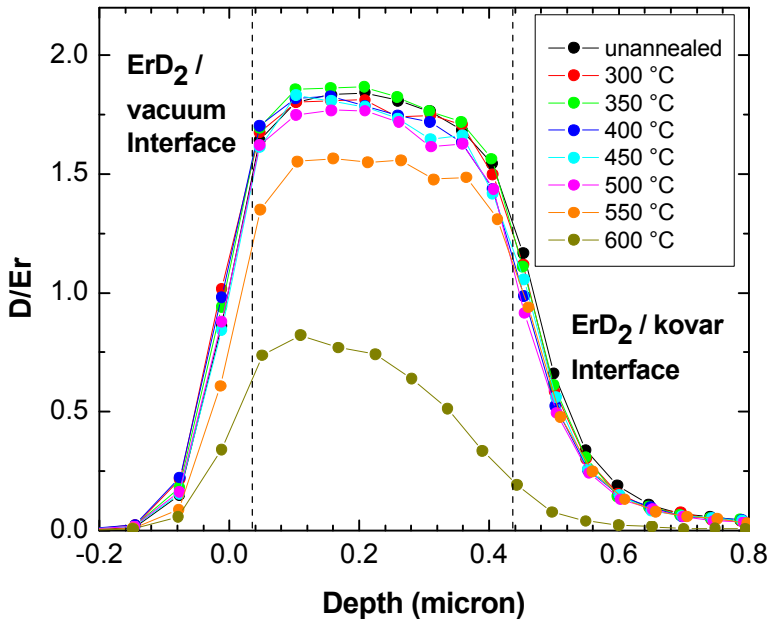
Isochronal anneals with sputtered Mo barrier

ErD_2 5 kÅ
Mo 2 kÅ
kovar

•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 D_2 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 ErD_2

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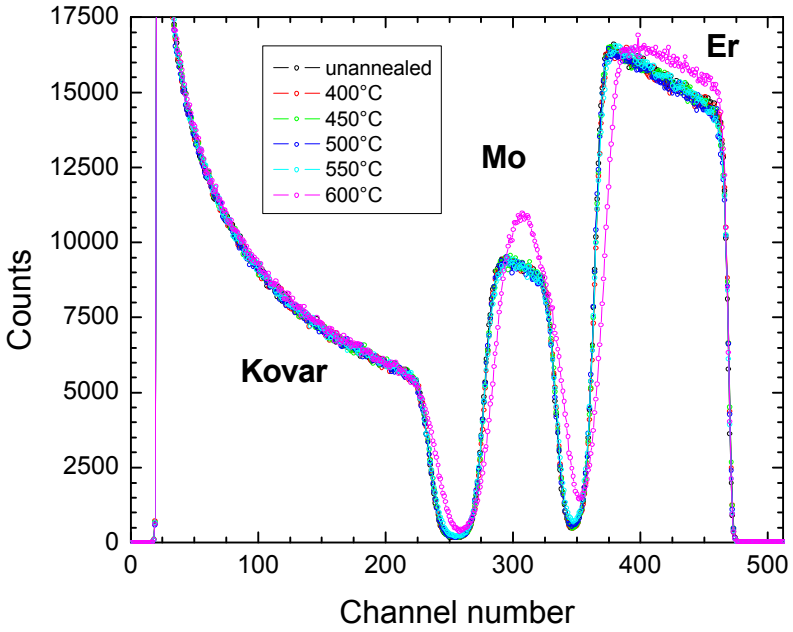
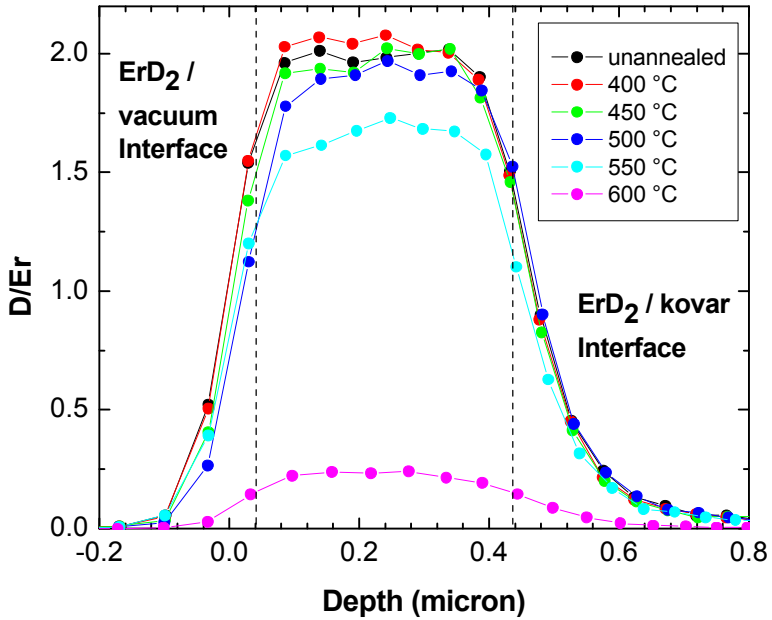
Isochronal anneals with e-beam Mo barrier

ErD_2 5 kÅ
Mo 2 kÅ
kovar

•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 D_2 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 ErD_2

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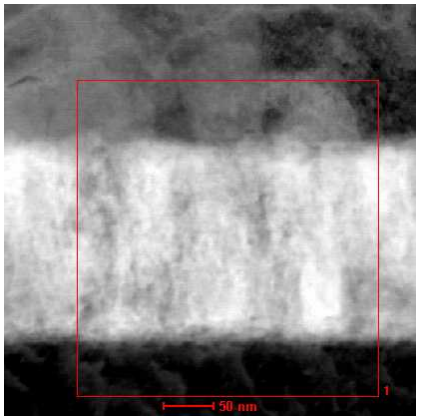
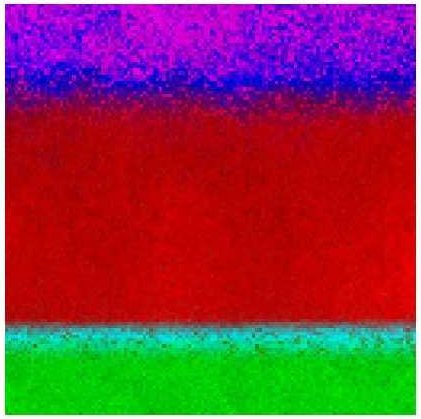
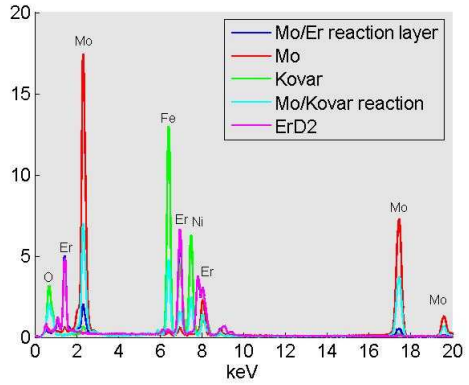
Microstructure differences in Mo films observed during scoping study*

- TEM EDS Luke Brewer 1822

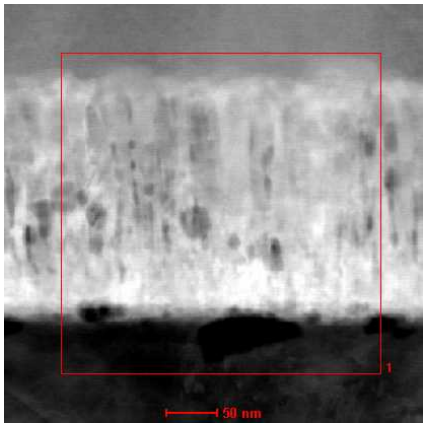
- Sample ID 23: kovar / 2 kÅ Mo (**e-beam evap**) / ErHD annealed at 564 °C for 2 hrs. in vacuum (~10^{-8} torr)

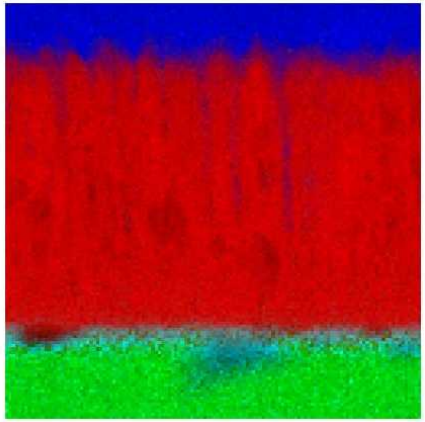


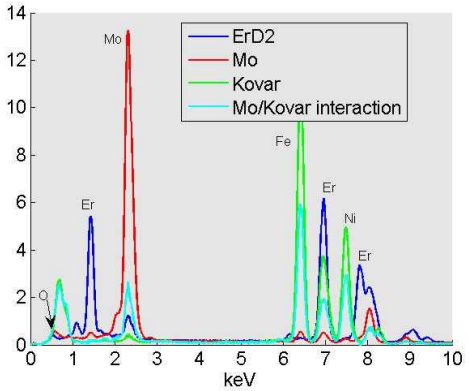




- Sample ID 42: kovar / 2 kÅ Mo (**sputter**) / ErHD annealed at 564 °C for 2 hrs. in vacuum (~10^{-8} torr)







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

*SAND2006-5864

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Conclusions

- Substantial mixing occurs at 450°C for Er/Kovar and 500 °C for ErD_2/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 ErD_2/kovar yield information about mixing
  - Diffusion model of Er with E_a = 2.1 eV and D_o = 0.071 cm^2/s
  - Assumes Er is moving through a ”static” matrix when matrix is actually changing

- Mo can act as diffusion barrier
  - ErD_2/kovar mixing evident at 500 °C
  - ErD_2/Mo(sputtering)/kovar mixing evident between 500-550 °C
  - ErD_2/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
  - B. Wampler, S. Van Deusen, S. King, R. Tissot, Luke Brewer, L. Espada, R. Goeke, Kathleen Hatch, Craig Tewell, & Firouzeh Jalali

- Scoping Study
  - L. Walla, M. Lopez, L. Espada, K. Hatch, S. King, C. Tewell, F. Jalali, R. Goeke, H. Peebles, C. Laduca, M. Courtney, F. McNamara, G. Moore, R. Herrick, R. Ohlhausen, R. Tissot, M. Rodriguez, W. Buttry, T. Ohlhausen, M. Rye, L. Brewer, B. Wampler, S. Van Deusen

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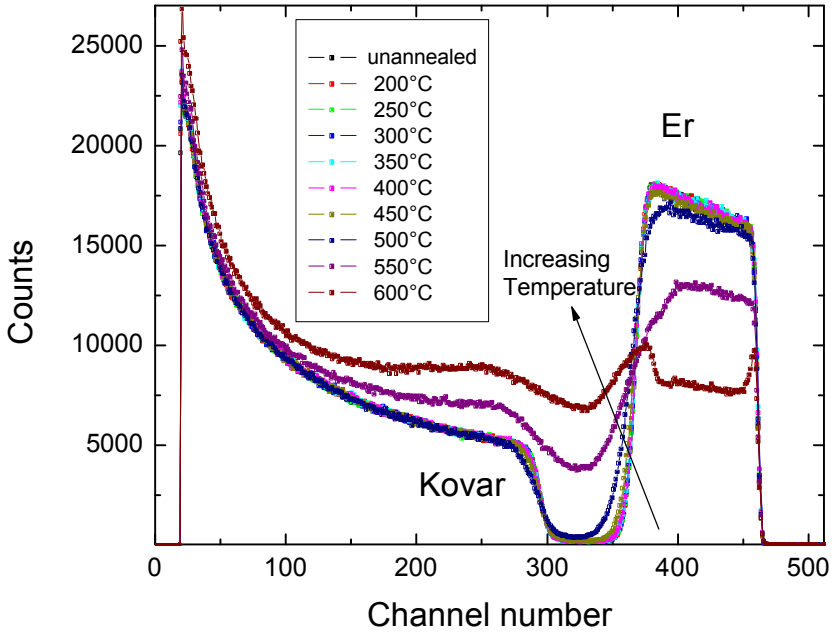
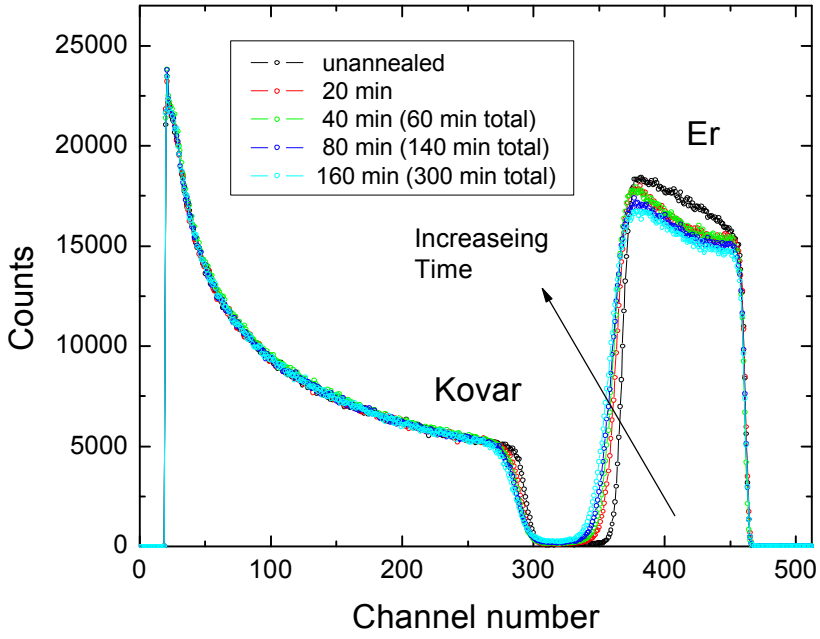
Isochronal and Isothermal anneals of Er/kovar

Er 5 kÅ Ambient & 450 °C
kovar

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



•**Isothermal** anneals at 450°C of 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
- O_2 or H_2O reaction from Er surface moving into film?

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