D loss as a function of temperature in ErD_2 films on kovar with and without an intermediate Mo diffusion barrier

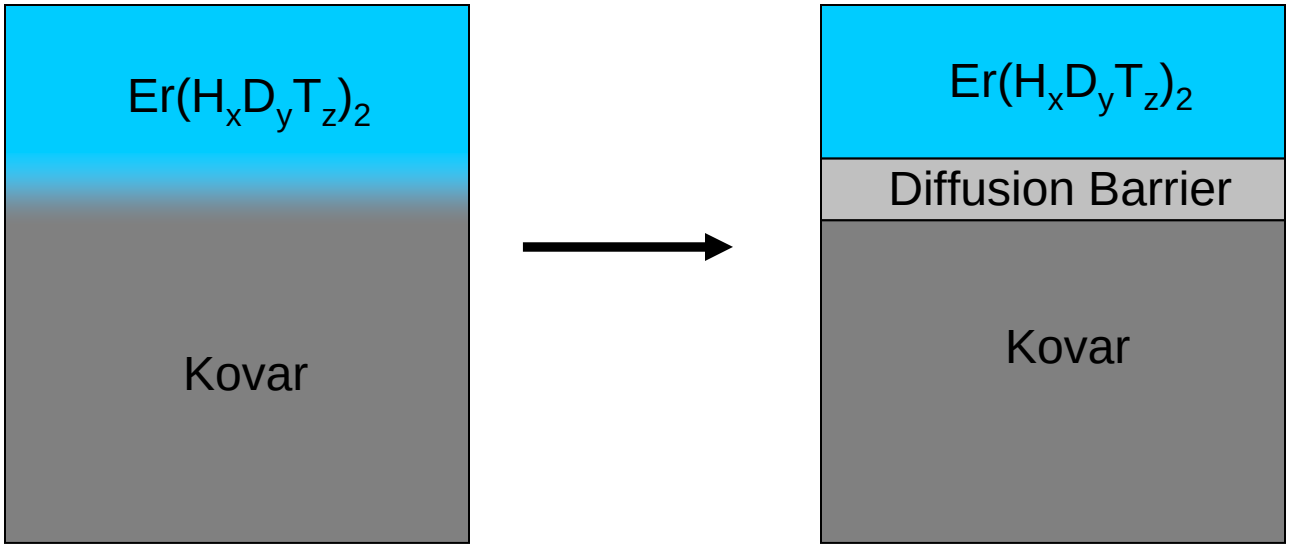
Dan Kammler, Bill Wampler, Stuart Van Deusen, Saskia King, Ralph Tissot, Luke Brewer, Loren Espada, and Ron Goeke

Sandia National Laboratories

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**

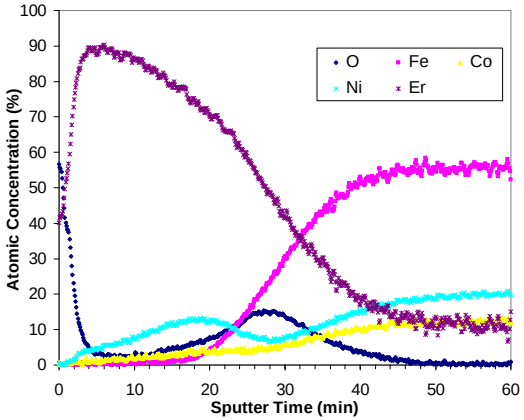
- **Diffusion barriers investigated to prevent mixing**

Mo was chosen as a diffusion barrier*

ErD_2 5 kÅ
kovar

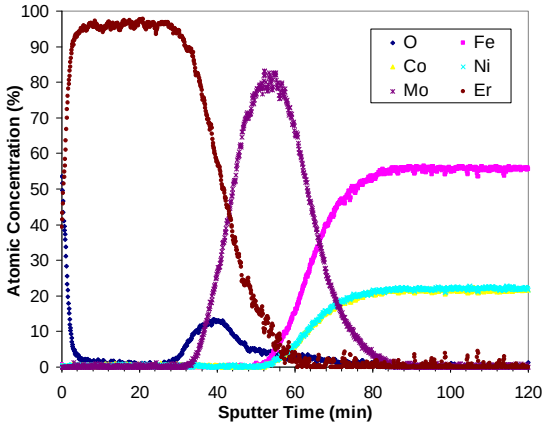
- Unknown phases in XRD pattern, Er_2O_3 present as well
- Auger data showed evidence of mixing
- Oxygen peak near Er/Kovar interface suggests possible oxide layer
- G:M was 0.703 on similar specimen

- 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

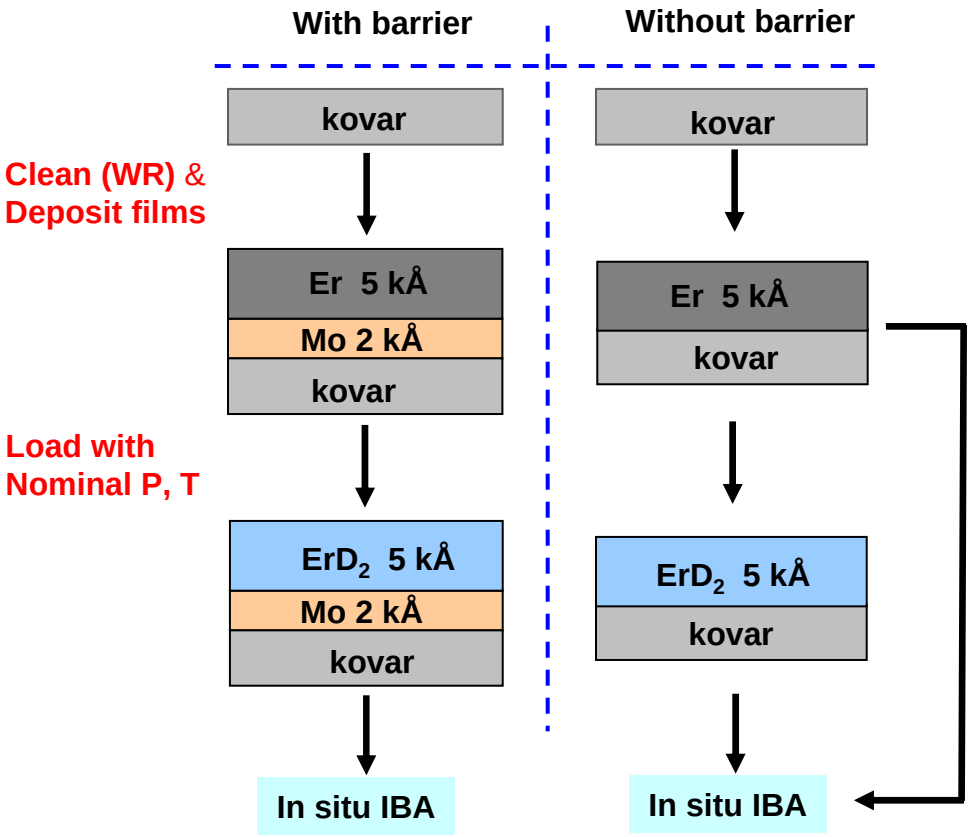
Sandia National Laboratories

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

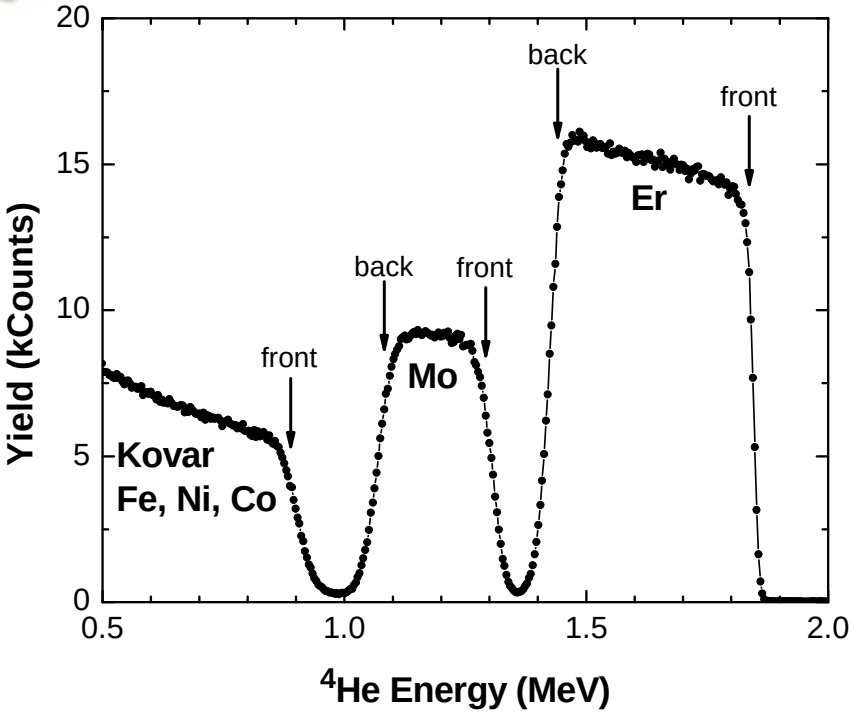
Outline of IBA Experiments

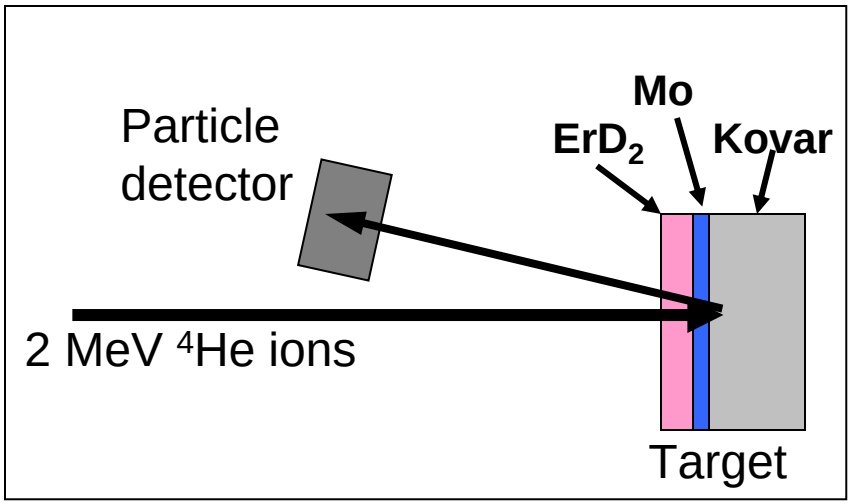
- Substrates
  - ¾” diameter kovar coupons
  - Clean and Degrease
  - Wet H_2 Fire and Vac Fire
- Film Deposition
  - Mo – 2 kÅ sputtered at ambient Temp
  - Mo – 2 kÅ ebeam evap at 450 °C
  - Er Evaporated at ambient & 450°C
- Loading
  - Coupons D_2 loaded in PCT using nominal conditions
- Characterization
  - RBS
  - NRA



Sandia National Laboratories

Rutherford Backscattering (RBS)

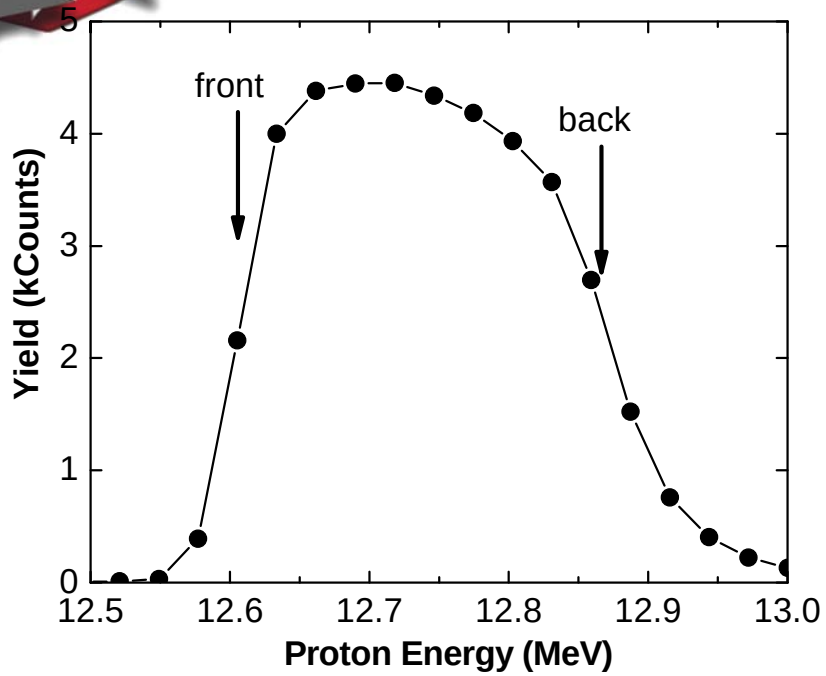


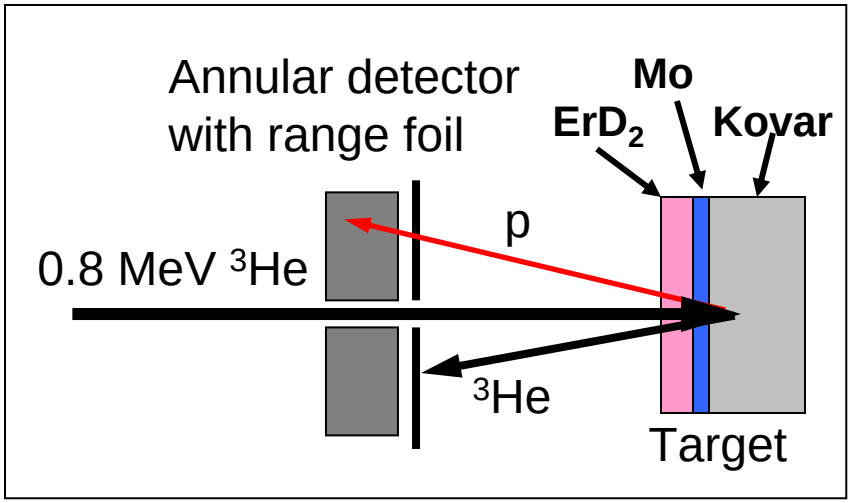


- Metals (Er, Mo, Kovar) are analyzed by Rutherford backscattering with 2 MeV ^{4}He.
- The energy spectrum of elastically scattered ^{4}He is measured.
- ^{4}He scattered from lighter elements and from greater depths reaches the detector with less energy.
- The energy scale is transformed to a depth scale using known stopping power.
- Yield is transformed to concentration using known scattering cross sections.
- Mixing at interfaces broadens the edges.

Sandia National Laboratories

Nuclear Reaction Analysis (NRA)



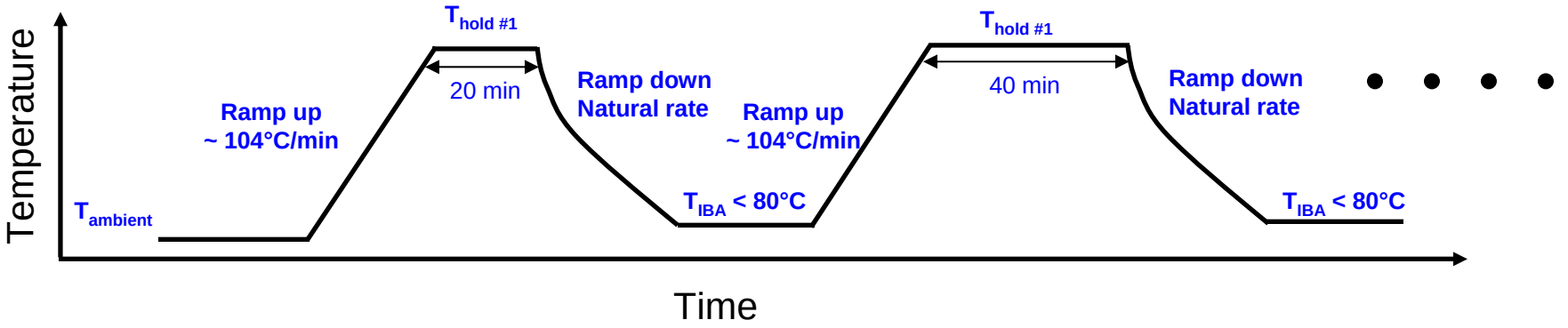


- The concentration of deuterium (D) versus depth was measured by D(^{3}He,p)α nuclear reaction analysis.
- An analysis beam of 0.8 MeV ^{3}He is directed onto the target.
- ^{3}He reacts with D in the tile producing protons with E ~ 12 MeV.
- The energy spectrum of the protons is measured by an annular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

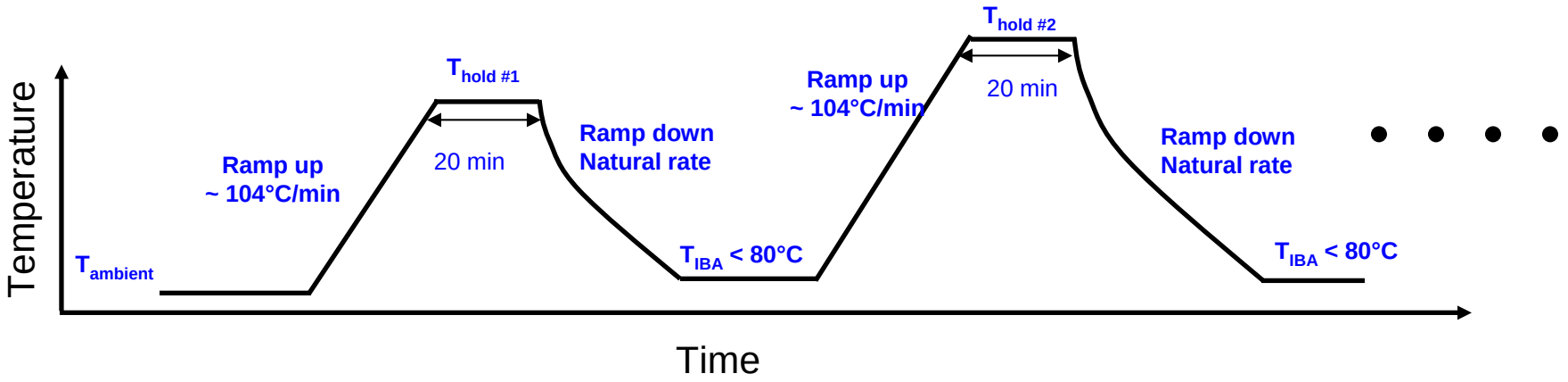
Sandia National Laboratories

Time/Temperature Schedule of In situ Anneals

- Isothermal Anneals



- Isochronal Anneals



Sandia National Laboratories

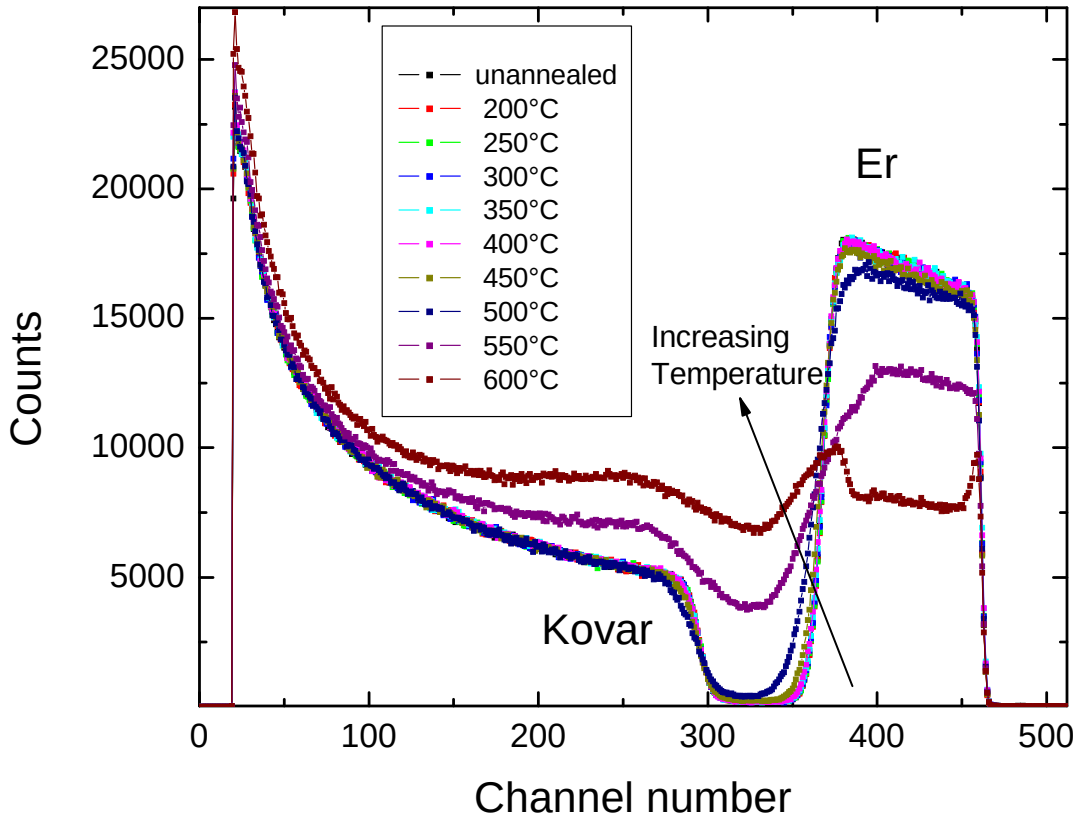
Sample Process & Characterization Summary

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



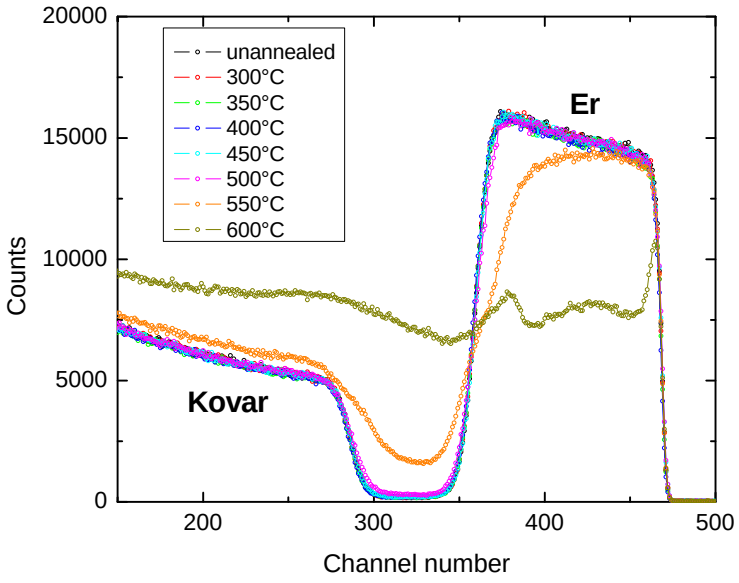
- Change evident between 400-450 °C

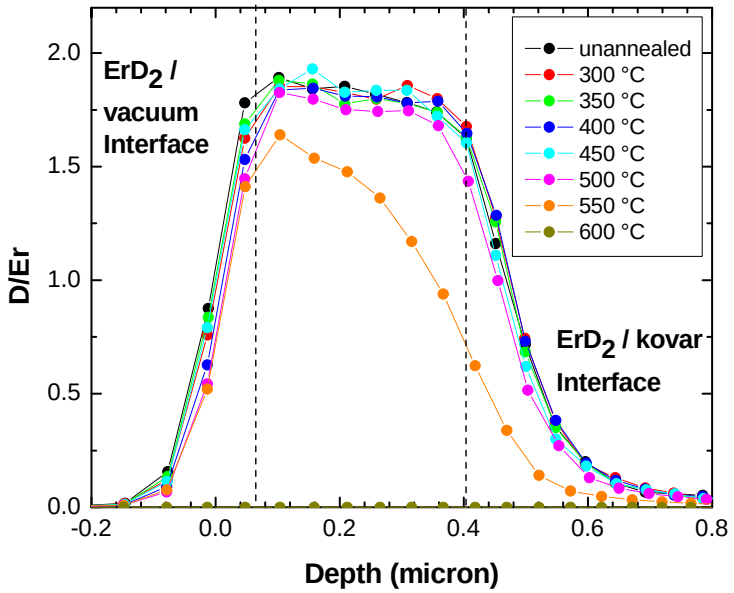
Sandia National Laboratories

Isochronal anneals of ErD_2/kovar

ErD_2 5 kÅ
kovar

- RBS & NRA data collected after Isochronal (20 min) anneals of Er deposited on kovar at 450°C and D_2 loaded (009)





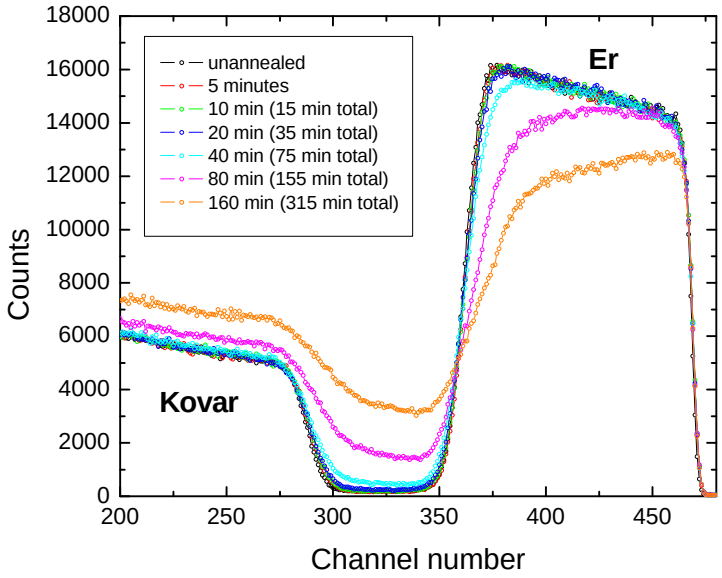
- Changes begin between 450-500°C and become rapid above 500°C.
- NRA spectra show D loss is from ErD_2/kovar interface
- D loss driven by mixing between kovar and ErD_2

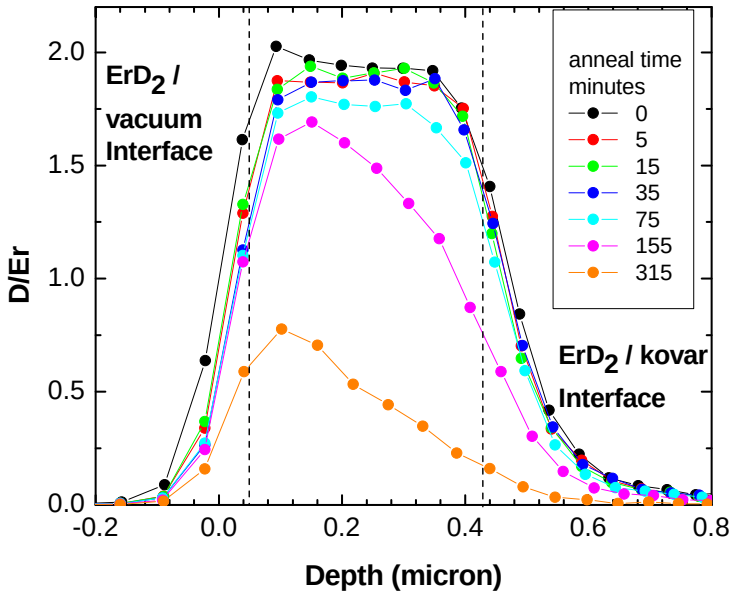
Sandia National Laboratories

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)





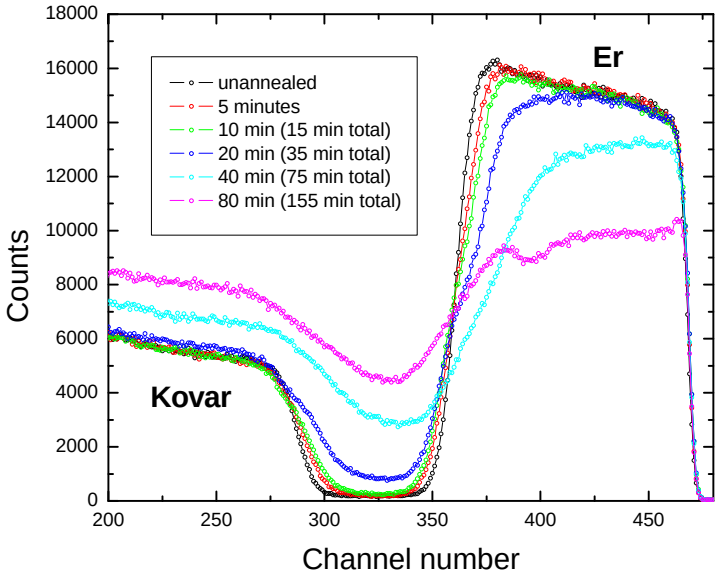
- Mixing is evident between 35 & 75 min.
- D loss predominantly from ErD_2/kovar interface
- D loss driven by mixing between kovar and ErD_2

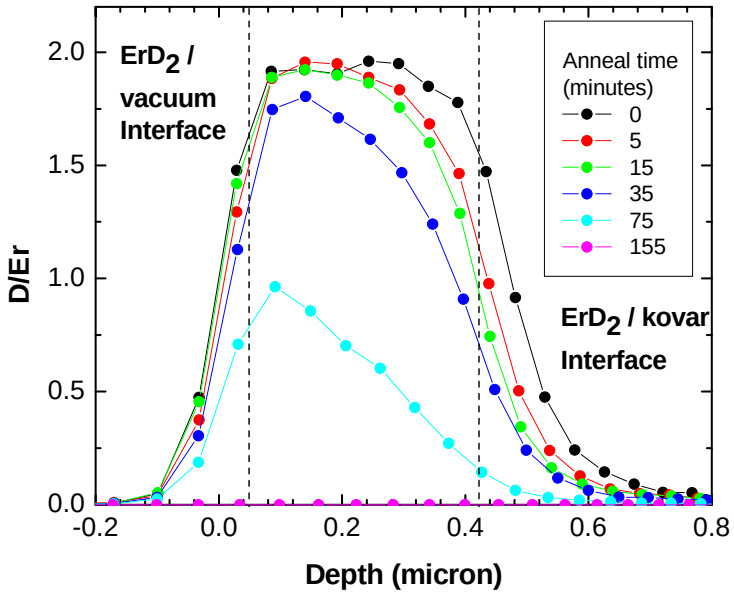
Sandia National Laboratories

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)

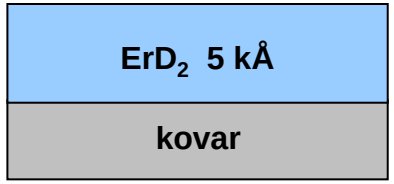


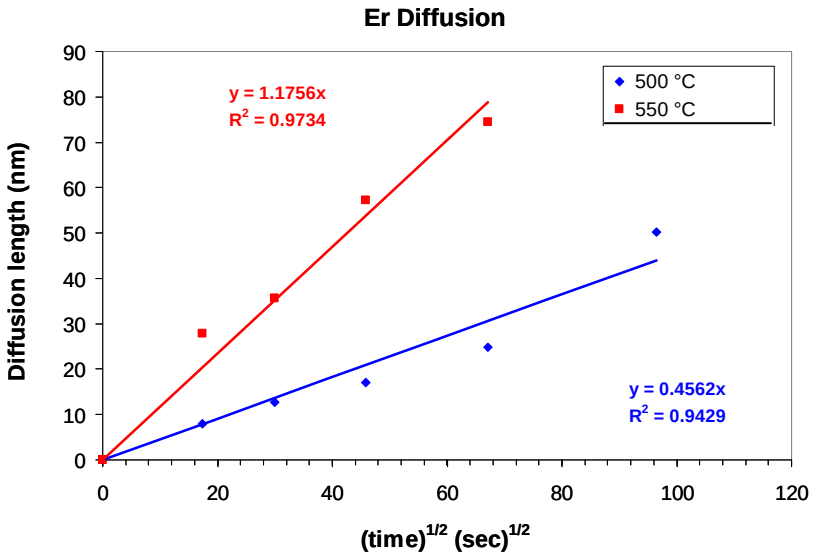


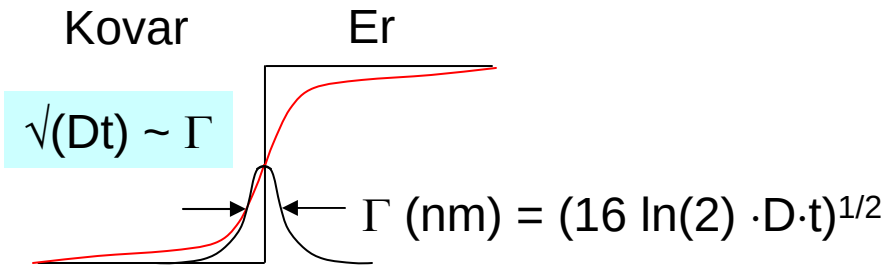
- Mixing is evident after only 5 min.
- D loss predominantly from ErD_2/kovar interface
- D loss driven by mixing between kovar and ErD_2

Sandia National Laboratories

Mixing of Er and kovar

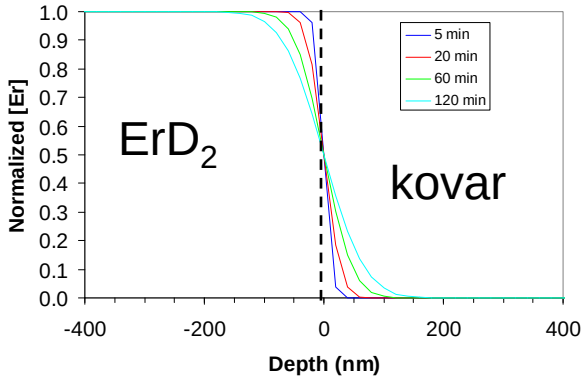




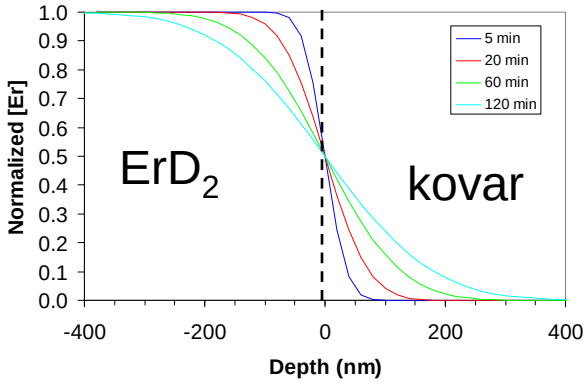


- $D = D_0 Exp(-E_a/kT)$
- E_a = 2.1 eV
- D_0=0.071 cm^2/s

[Er] for T = 500 °C



[Er] for T = 550 °C



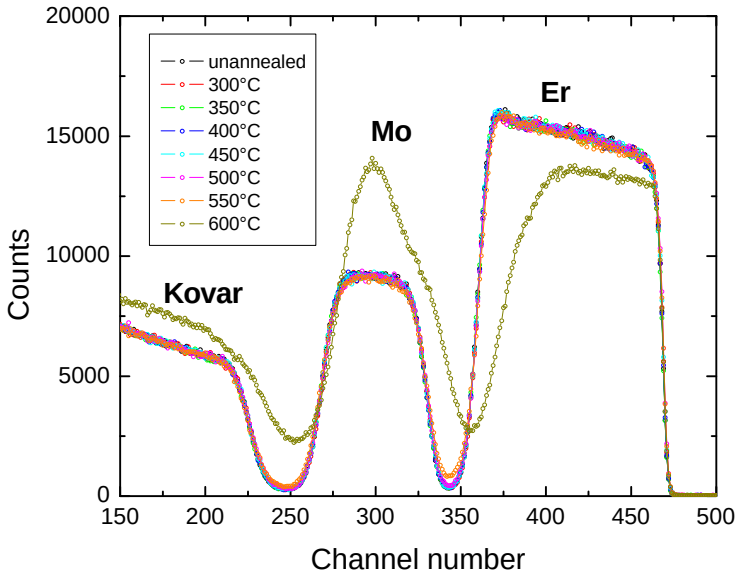
- We're assuming Er is moving through a "static" matrix when in reality it's constantly changing

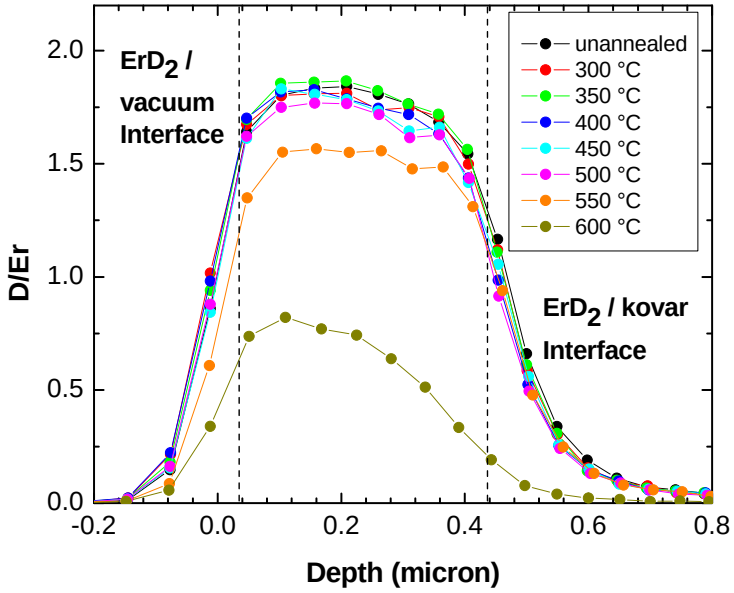
Sandia National Laboratories

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





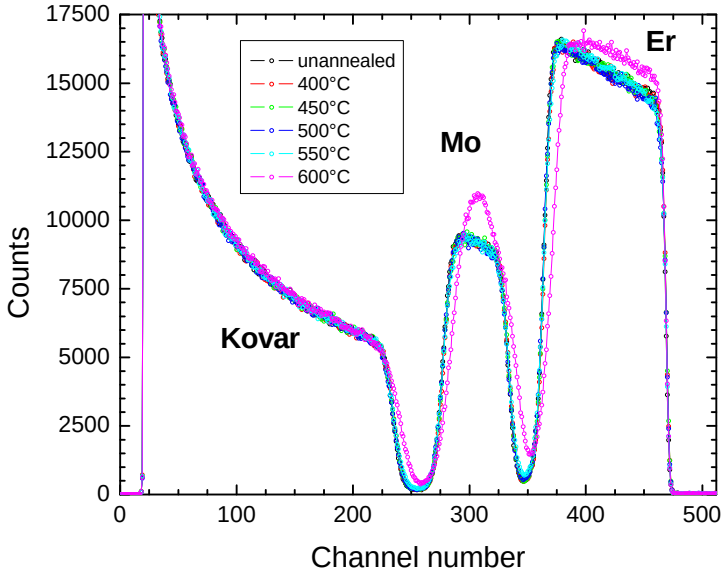
- Diffusion through Mo begins between 500-550°C
- D loss begins between 500-550°C but is more uniform throughout film
- D loss is driven by thermal decomposition of ErD_2

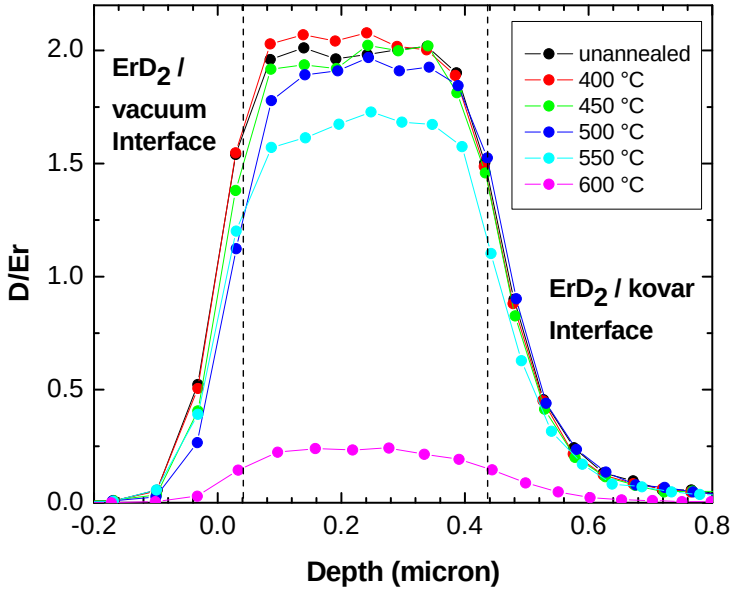
Sandia National Laboratories

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





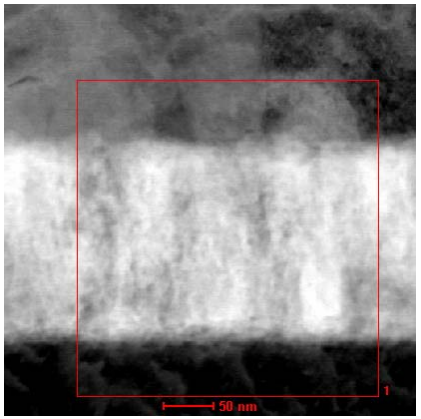
- Diffusion through Mo begins above 550°C
- D loss begins between 500-550°C and is uniform throughout film
- D loss is driven by thermal decomposition of ErD_2

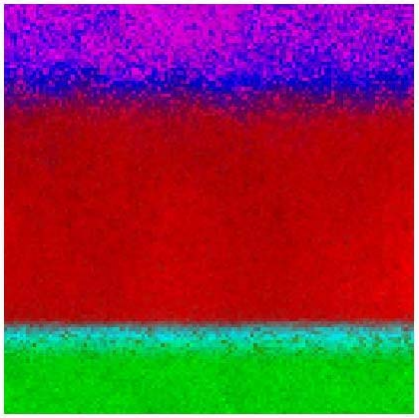
Sandia National Laboratories

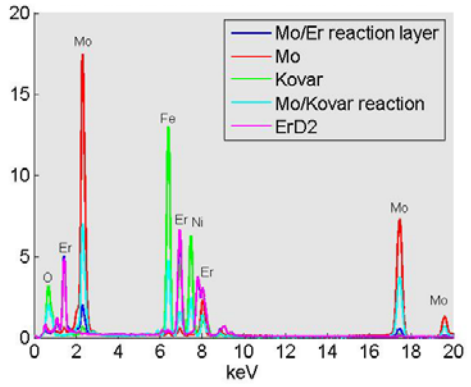
Microstructure differences in Mo films observed during scoping study*

- TEM EDS Luke Brewer 1822

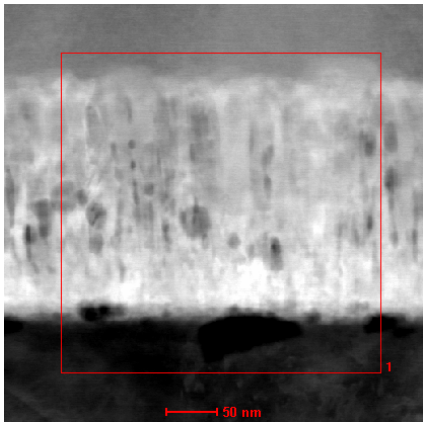
- Sample ID 23: kovar / 2 kÅ Mo (**e-beam evap**) / ErHD annealed at 564 °C for 2 hrs. in vacuum (~10^{-8} torr)

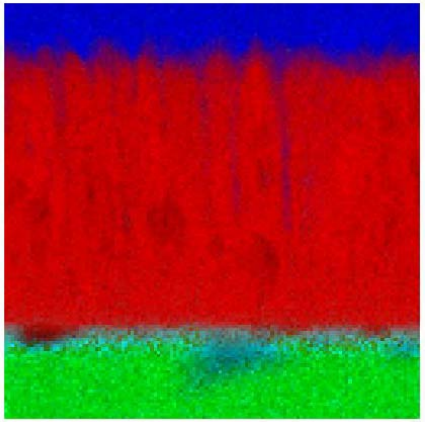


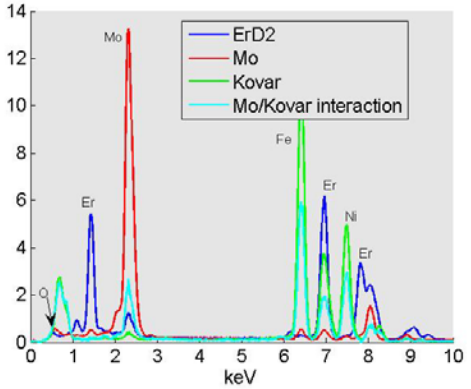




- Sample ID 42: kovar / 2 kÅ Mo (**sputter**) / ErHD annealed at 564 °C for 2 hrs. in vacuum (~10^{-8} torr)







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

*SAND2006-5864

Sandia National Laboratories

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

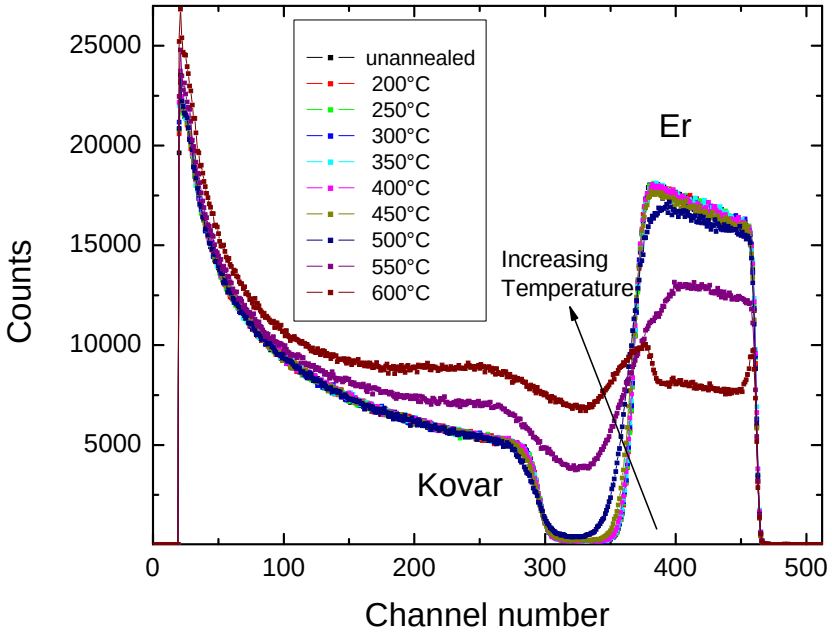
- Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

Sandia National Laboratories

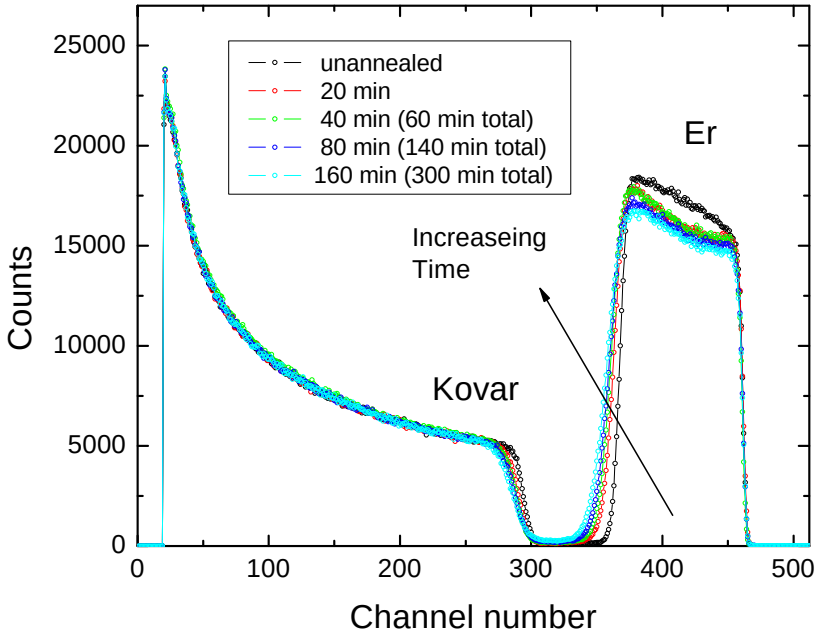
Isochronal and Isothermal anneals of Er/kovar

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?

Sandia National Laboratories