

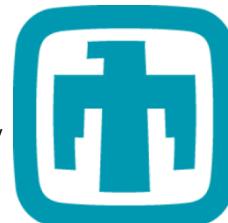
Direct observation of effective atomic diffusion distances in Zr/2Al multilayers due to self-propagating reactions

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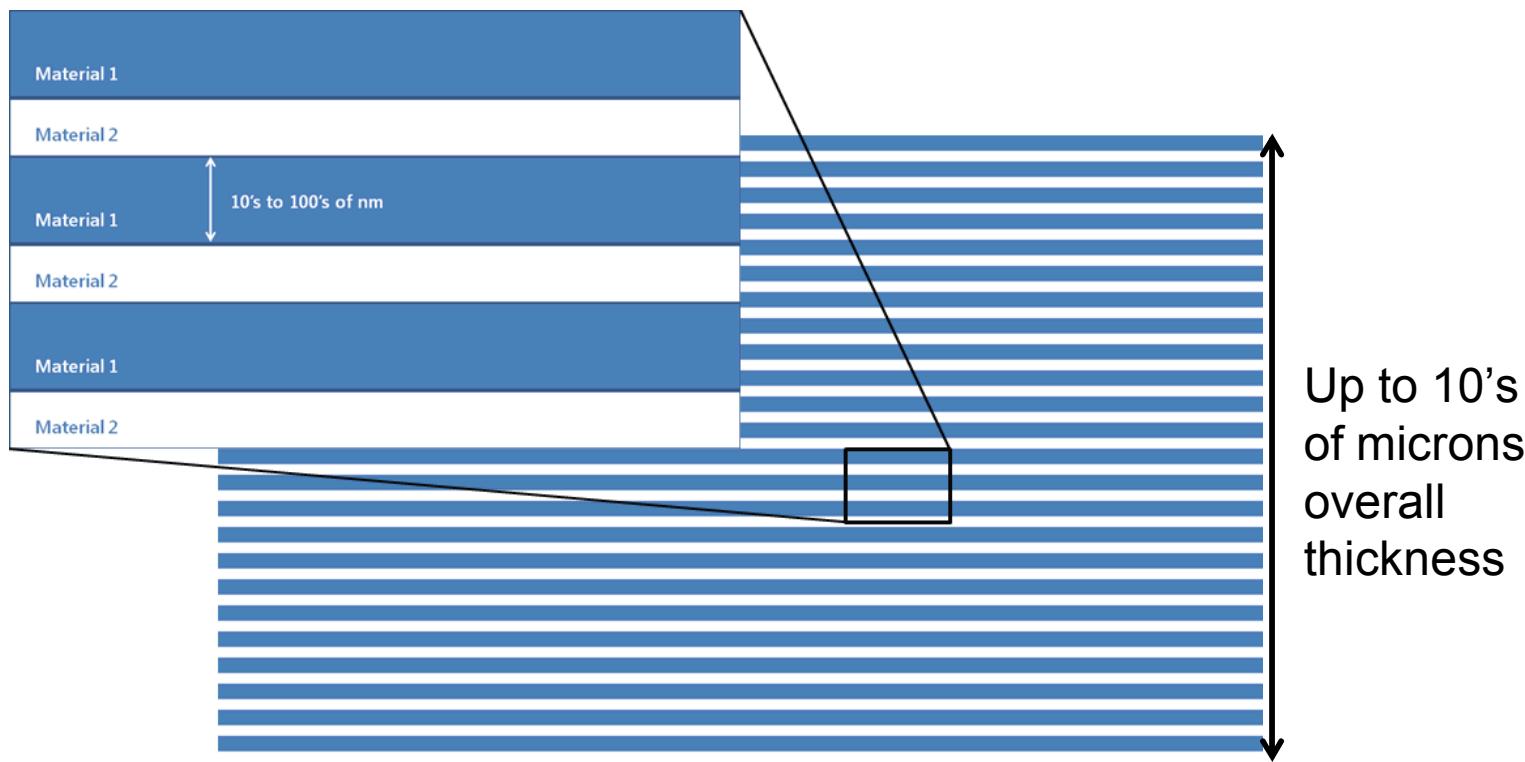


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Experimental Material

Zr/2Al Nanolaminates

- $Zr + 2Al \rightarrow ZrAl_2; \Delta H_{exp} = -46 \frac{kJ}{mol_{atoms}}$
(de Boer, Boom, Mattens, Miedema, Niessen, *Cohesion in Metals*, 1988)
- Typical design of sputtered reactive foils
 - Used extensively by Weihs, Adams, Rogachev, and others
 - Macroscale stacks of nanometric metal layers
 - Clean interfaces, high purity materials



Nanolaminates

Typical Reaction Progression

- Atoms diffuse to center line of neighboring reactant layer
- Final phase formed once this distance is traveled
- Can other mechanisms affect diffusion distance?
 - Dissipative thermodynamics
 - High temperature diffusion

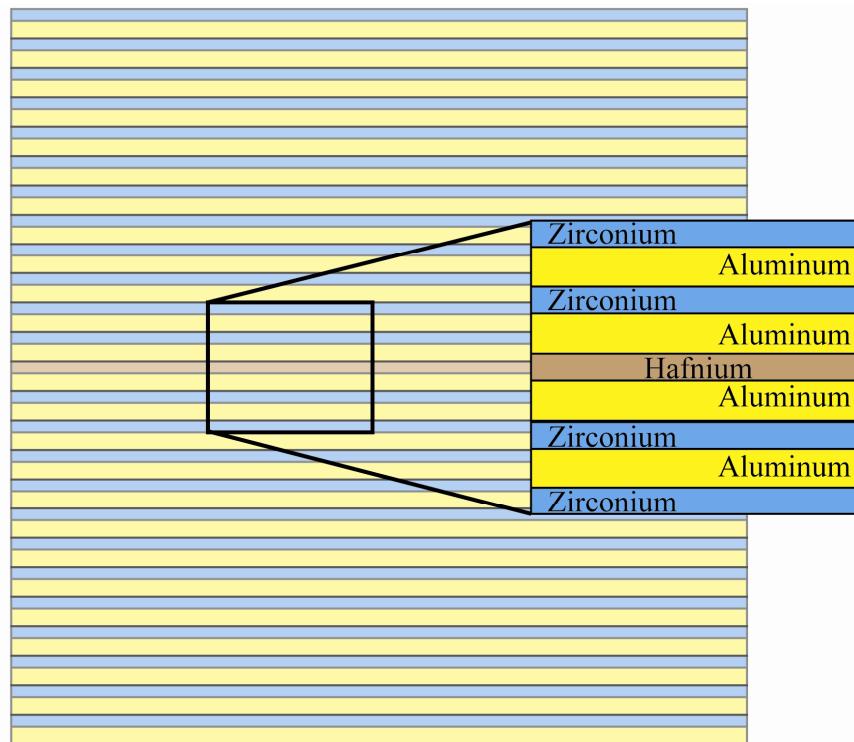
The diagram illustrates the typical reaction progression of nanolaminates. It shows three stages: 'As-Deposited', 'During Reaction', and 'Reaction Completed'. The 'As-Deposited' stage shows a stack of three alternating blue and yellow layers. A double-headed arrow between the top and middle blue layers is labeled 'Nominal Diffusion Distance'. An arrow points from this stage to the 'During Reaction' stage. The 'During Reaction' stage shows the same stack of layers, but the yellow layers have been partially converted into green layers, indicating a reaction. Two wavy arrows on the right side of the stack are labeled $\dot{Q} > 0$, representing heat generation. An arrow points from the 'During Reaction' stage to the 'Reaction Completed' stage. The 'Reaction Completed' stage shows the entire stack of layers now uniformly green, representing the final reaction product. The background features horizontal dashed lines corresponding to the layer interfaces.

Marker Layer Design

Zr+(Hf)/2Al Nanolaminates

Compare ph
properties
DSC results

- Hafnium replaces Zr at a single layer
- Hafnium and Zr are miscible with no distinct intermetallic phases
- Similar chemistry and product phases with Al

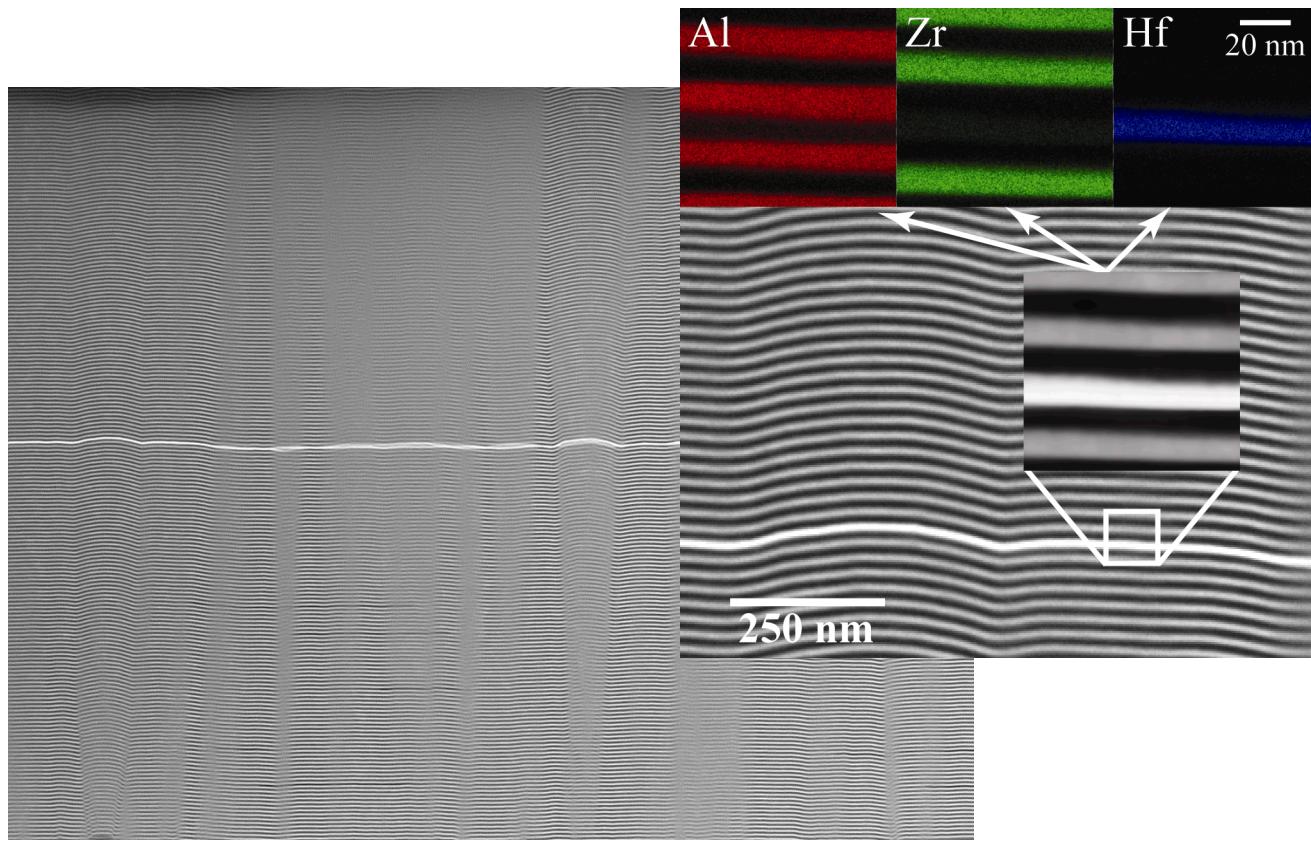


ZrAl ₂	T _m = 1660 °C	HfAl ₂	T _m = 1650 °C
	ΔH = -46 kJ/mol		ΔH = -48 kJ/mol
hP12	a = 0.52824	hP12	a = 0.525
	b = 0.52824		b = 0.525
	c = 0.87482		c = 0.868
Zr ₂ Al ₃	T _m ≈ 1590 °C	Hf ₂ Al ₃	T _m = 1660 °C
	ΔH = -47 kJ/mol		ΔH = -48 kJ/mol
oF40	a = 0.9601	oF40	a = 0.9529
	b = 1.3906		b = 1.3763
	c = 0.5574		c = 0.5525

Marker Layer Design

Zr+(Hf)/2Al Nanolaminates

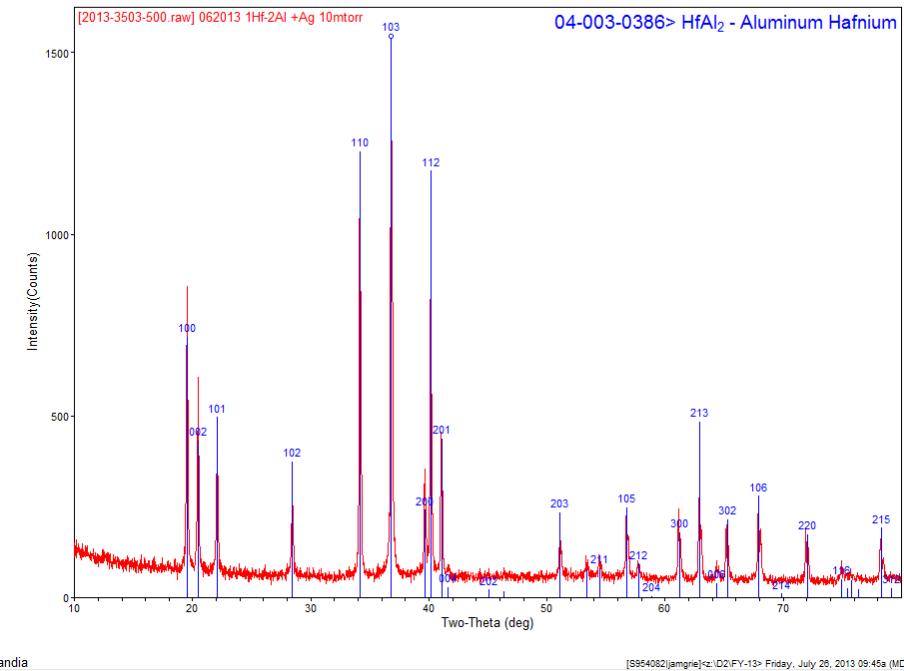
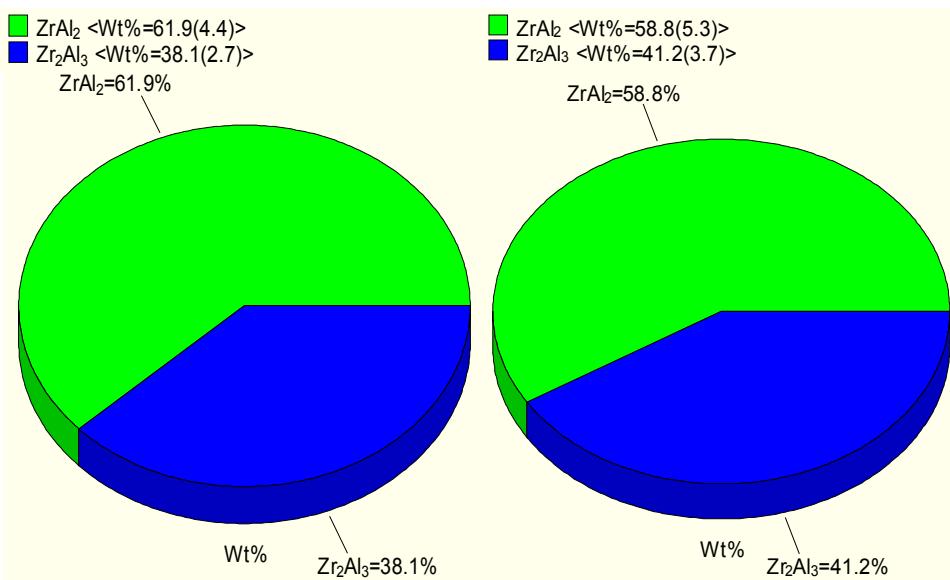
- Marker layer distinct
- Clearly resolvable with z-contrast and EDS in TEM



Phase Identification

Zr/2Al and Hf/2Al Standards

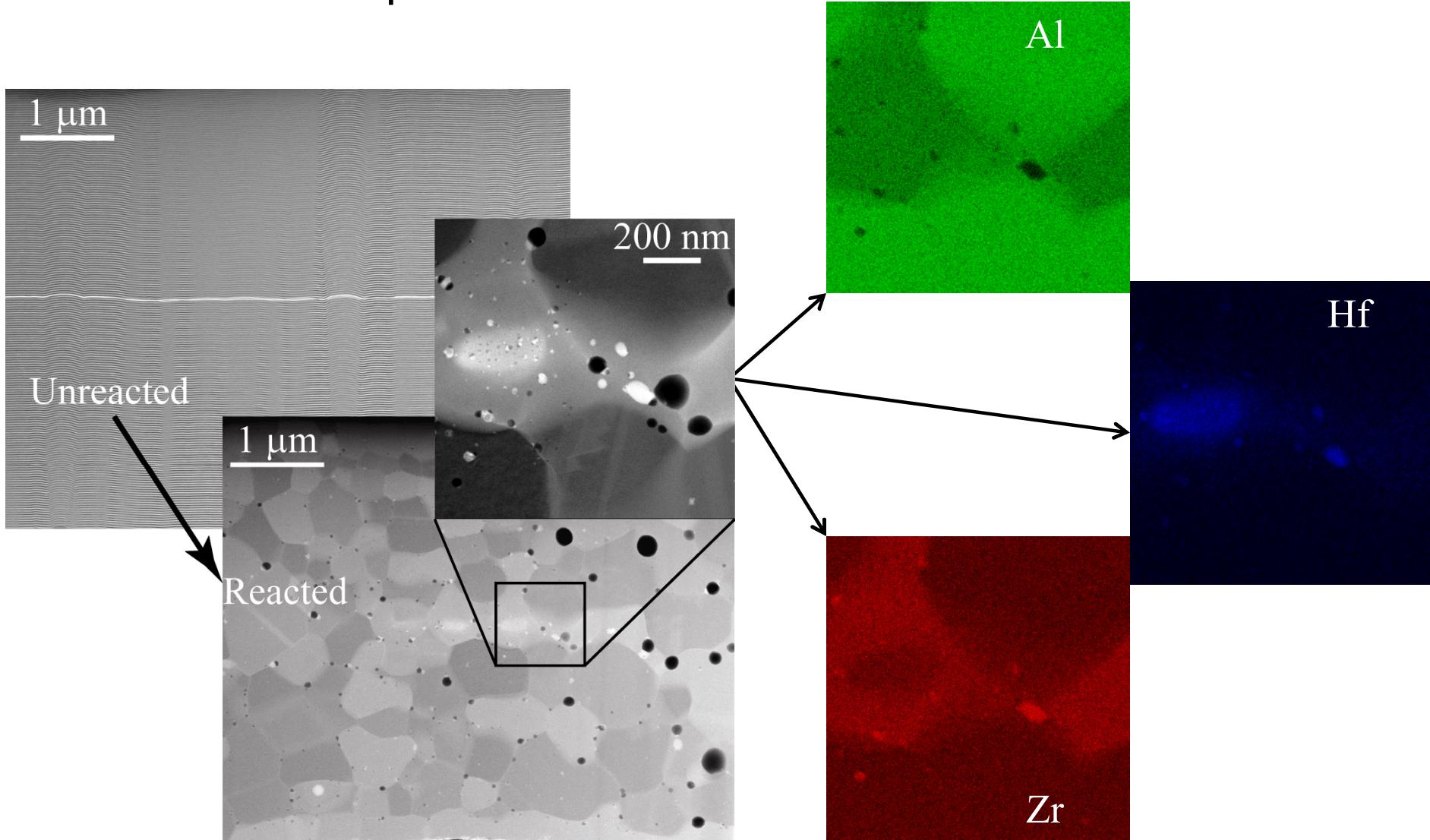
- Zr/2Al films reacted in vacuum (10 mTorr)
- ZrAl₂ (~60% wt%) and Zr₂Al₃ (~40% wt%) phases identified by XRD
- Hf/2Al films reacted in vacuum (10 mTorr)
- Phase pure HfAl₂



Marker Layer Design

Zr+(Hf)/2Al Nanolaminates

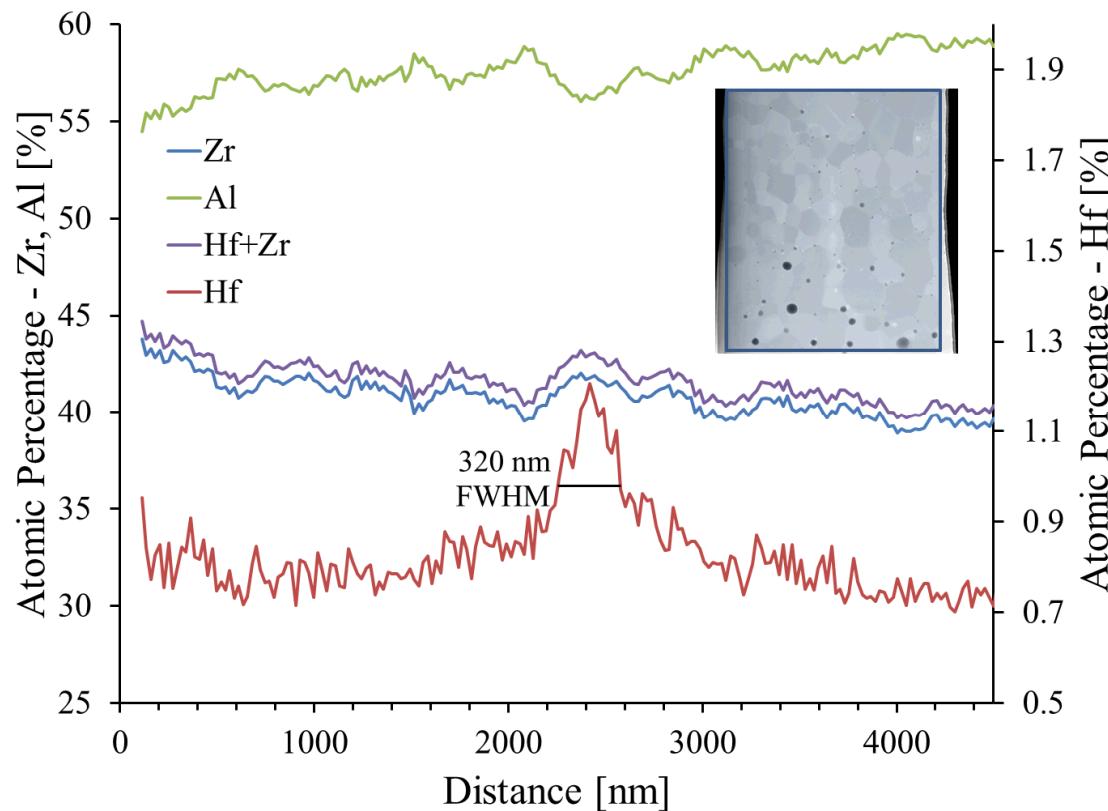
- Reaction disperses Hf marker material



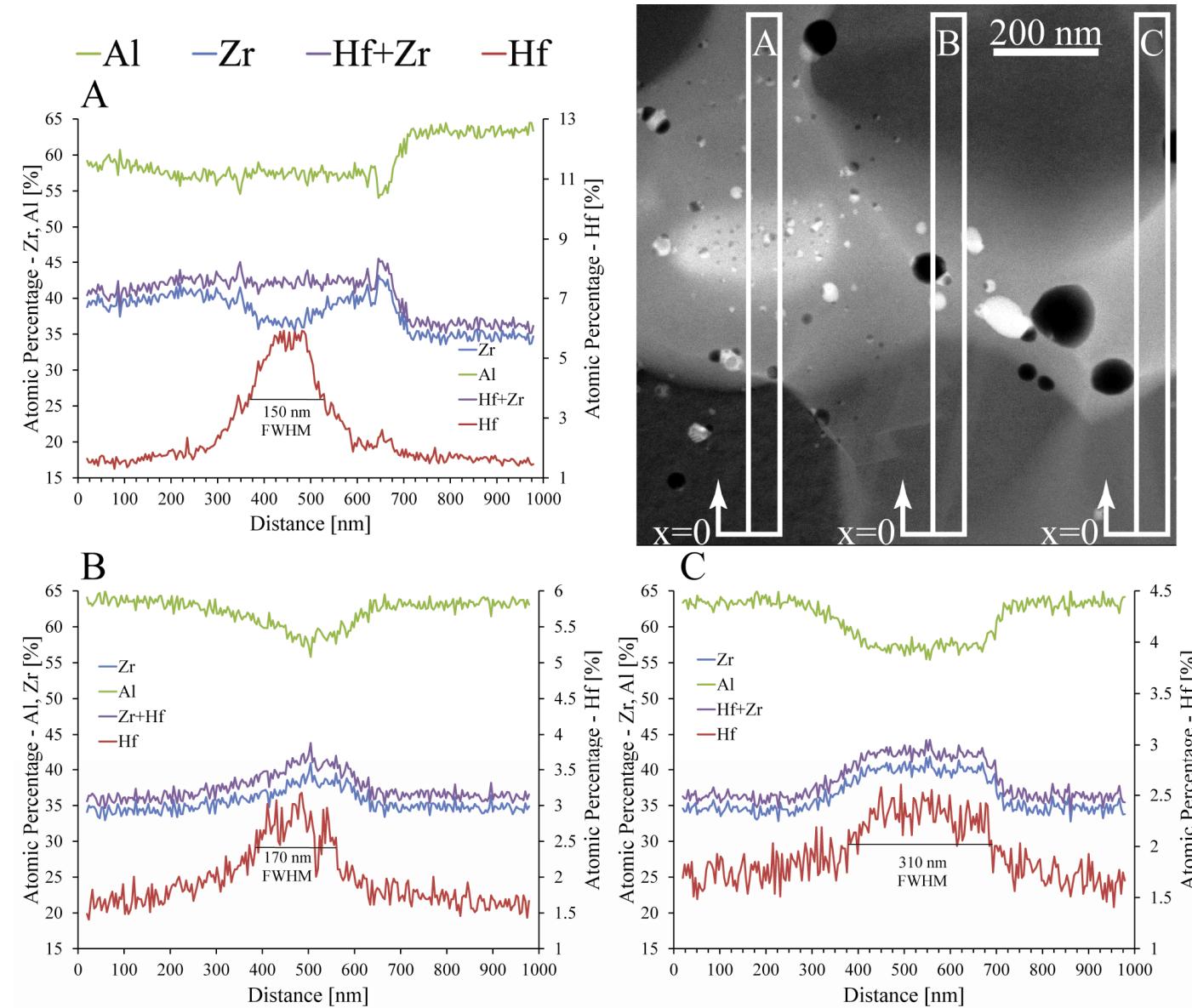
Marker Layer Design

Zr+(Hf)/2Al Nanolaminates

- Reaction disperses Hf marker material
- 14 kx magnification – $5 \times 5 \mu\text{m}$ ROI
- Probed through EDS and SIMS



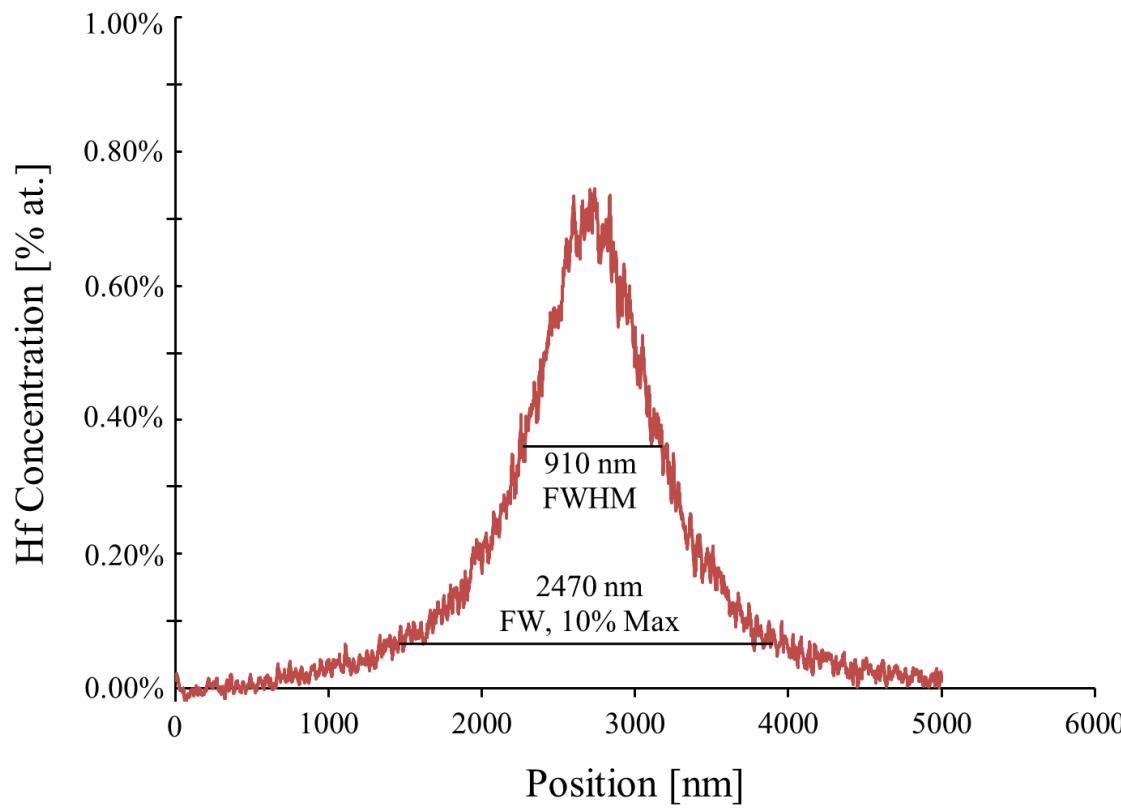
Variation at smaller length scales



Marker Analysis by SIMS

Zr+(Hf)/2Al Nanolaminates

- Sputter area = $200 \times 200 \mu\text{m}^2$
- Analysis area = $50 \times 50 \mu\text{m}^2$ – much greater area than EDS
- Hf-baseline subtracted from signal

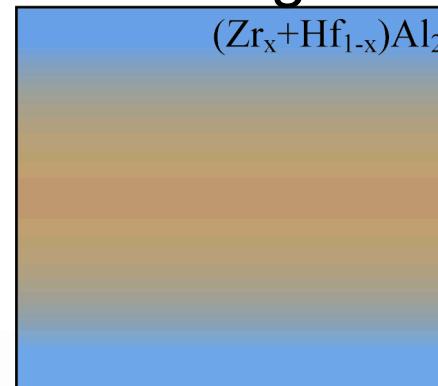


Diffusion model – Assumed progression

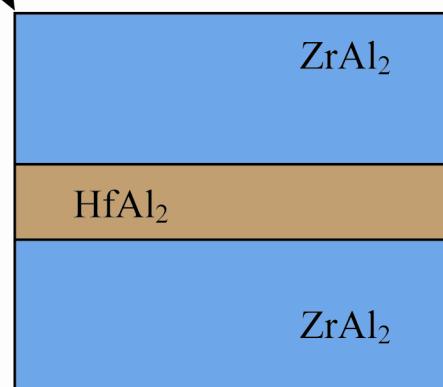
As-deposited state



Final configuration



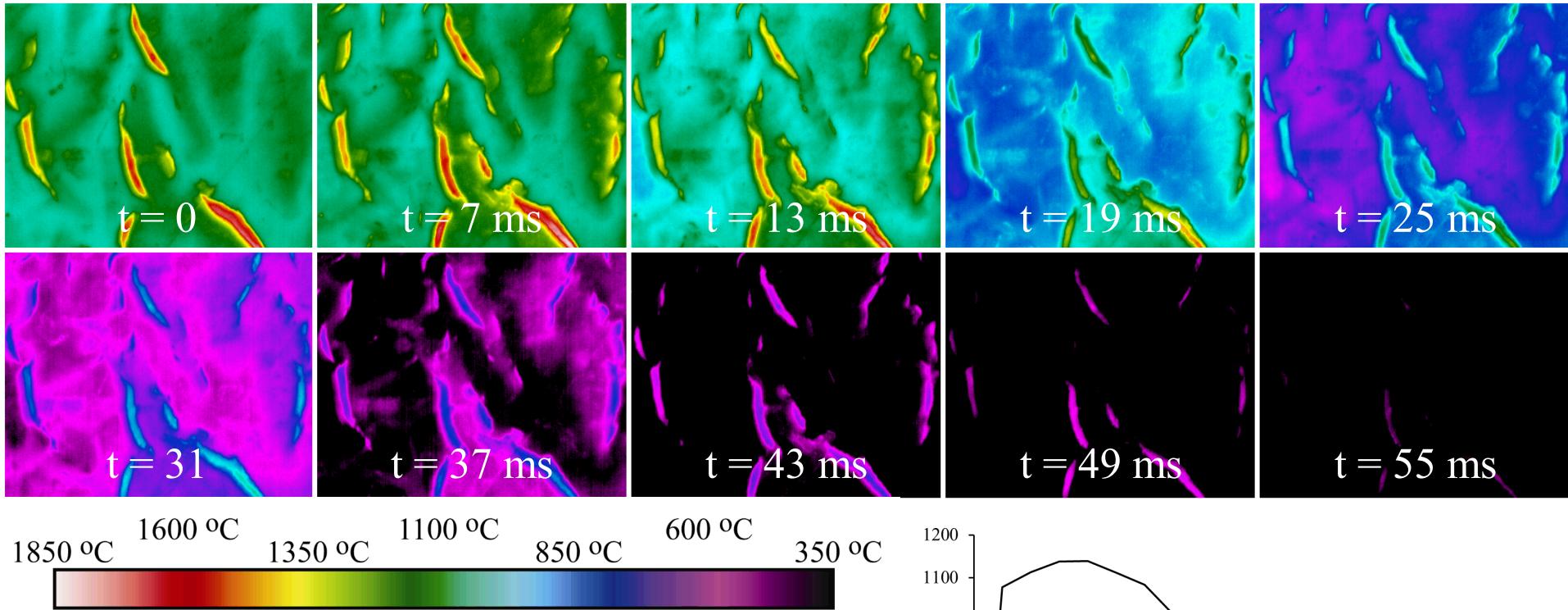
Reaction occurs



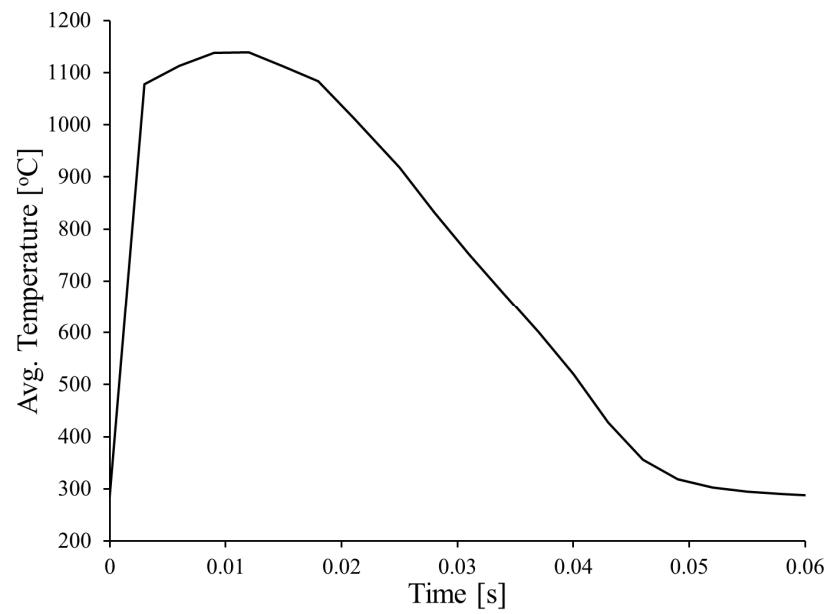
Solid-state diffusion at elevated temperatures

Reaction completed

IR imaging of temperature history

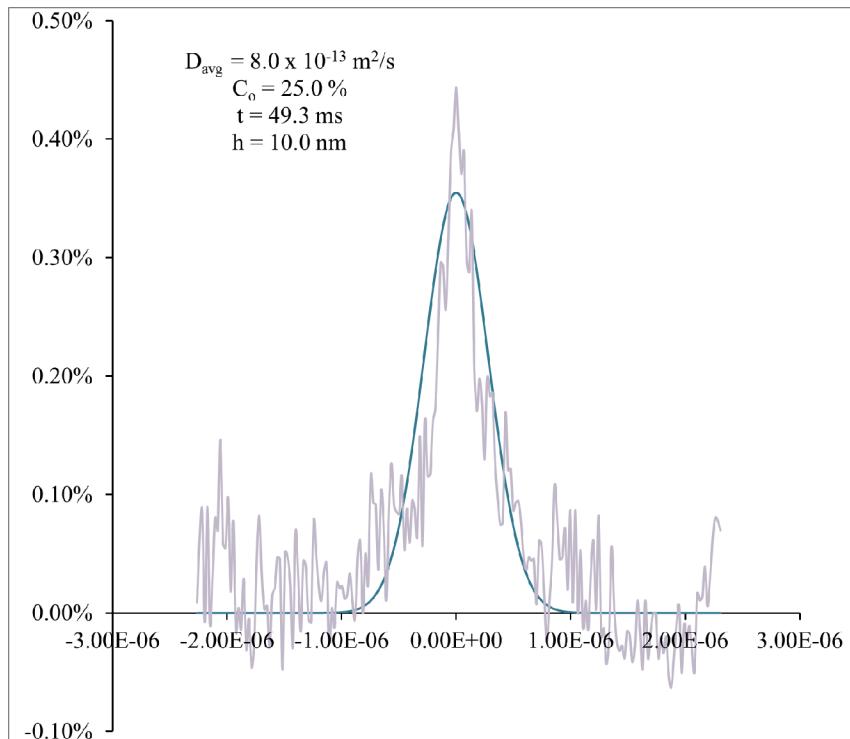


- Plot is average meas. temp of surface in image (4.8 x 3.8 mm)
- Time average over 46 ms is 690 °C (963 K)
- Information for comparison to best fit results from diffusion model



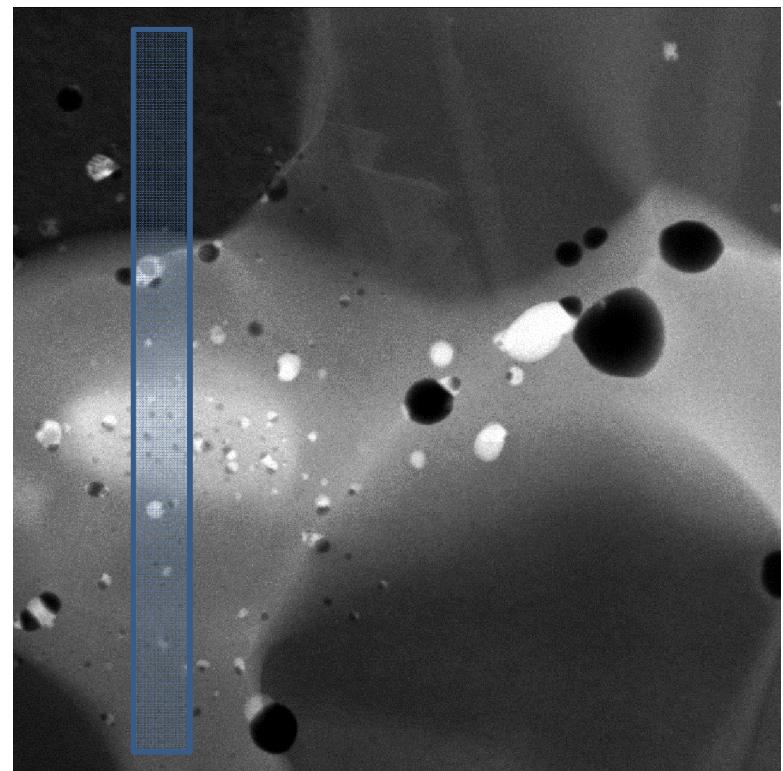
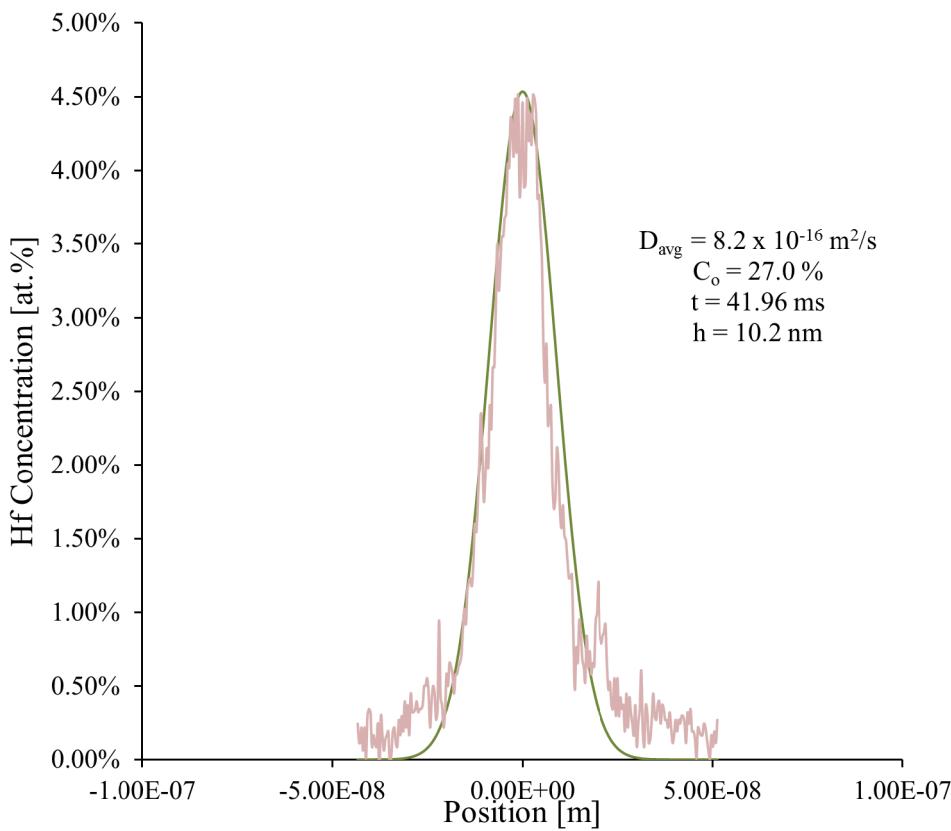
Diffusion model – Compare to EDS data

- Integration of EDS Hf signal over full 14 kx image (5x5 μm)
- Fits do not match well with simple diffusion model and assumptions



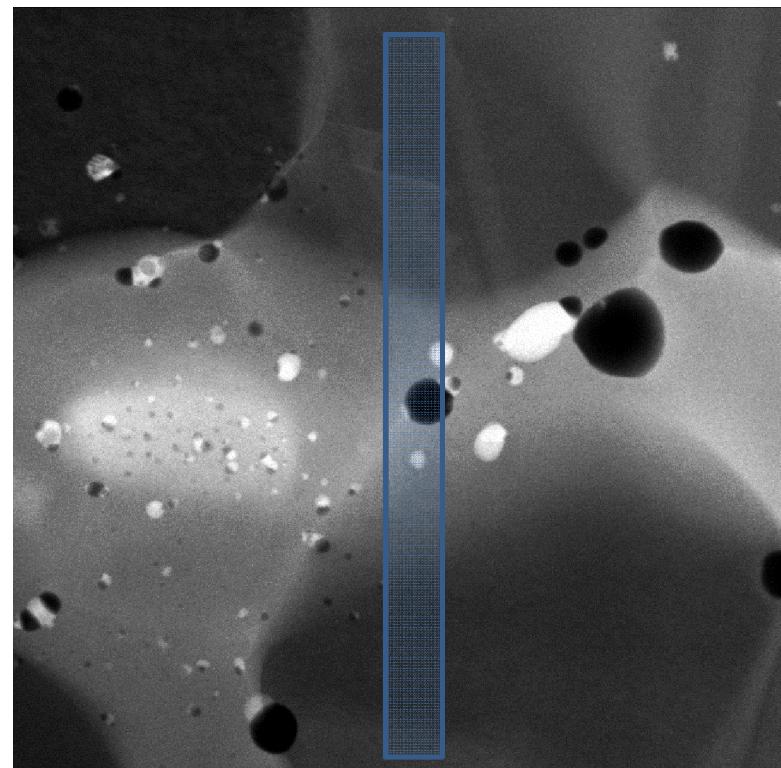
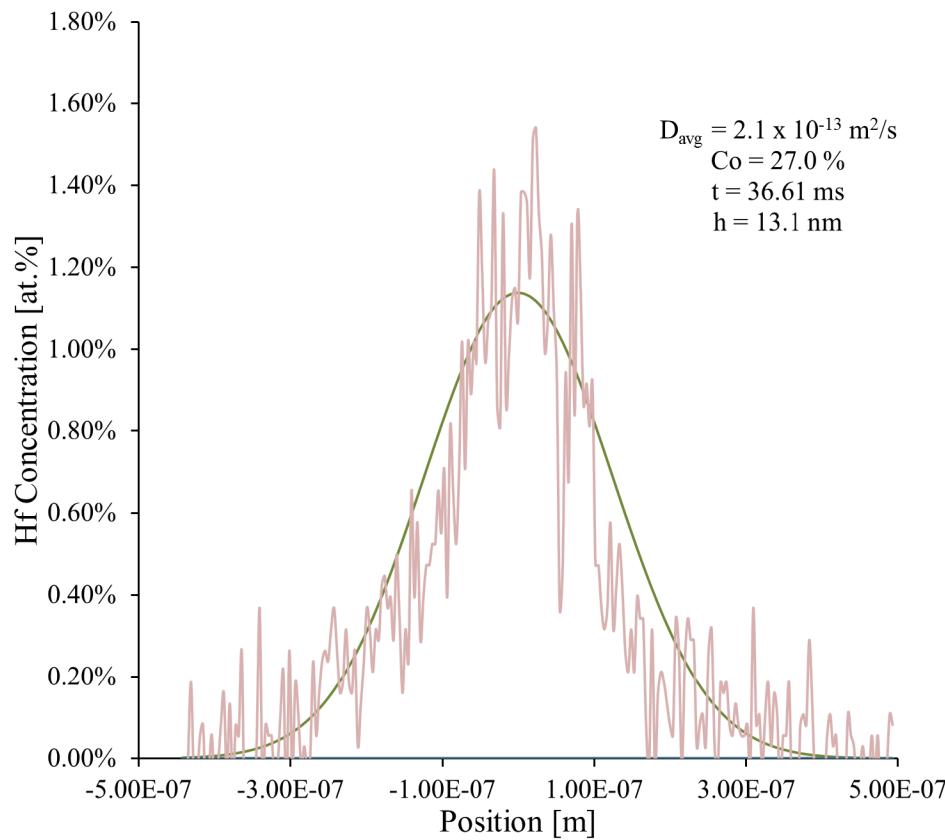
Diffusion model – Compare to EDS data

- Integrated profile across 40 nm x 1000 nm path (shown)
- Best fit $D = 8.2 \times 10^{-16} \text{ m}^2/\text{s}$



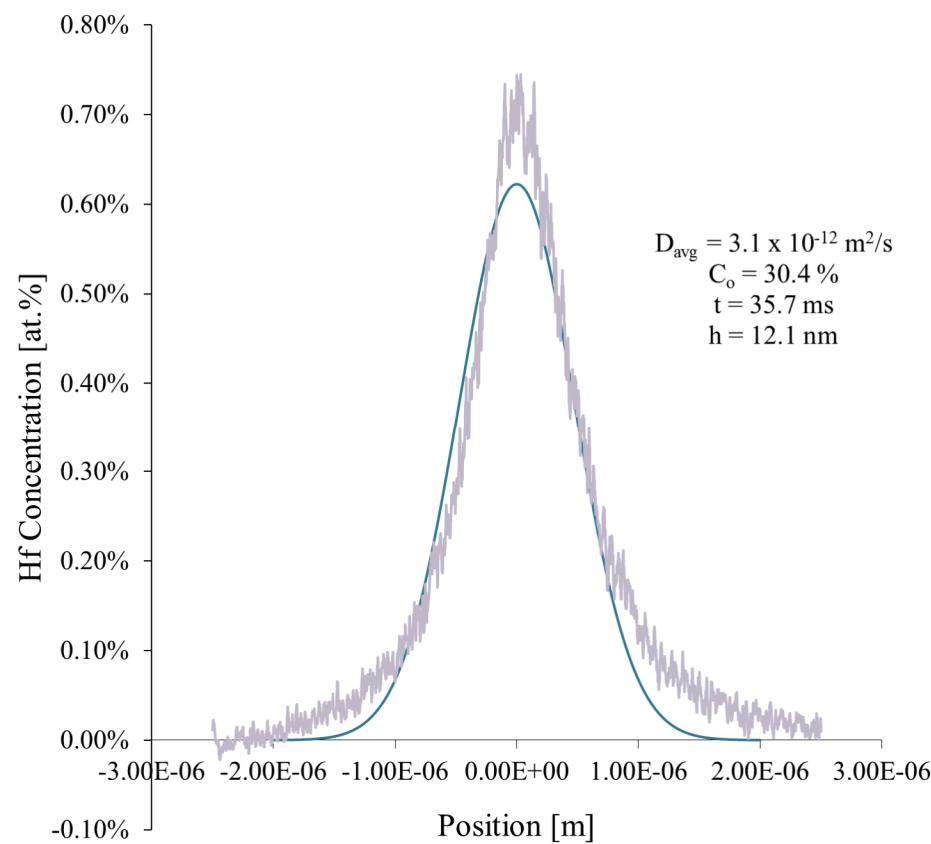
Diffusion model – Compare to EDS data

- Integrated profile across 40 nm x 1000 nm path (shown)
- Best fit $D = 2.1 \times 10^{-13} \text{ m}^2/\text{s}$



Diffusion model – Compare to SIMS data

- Best fit $D = 3.1 \times 10^{-12} \text{ m}^2/\text{s}$
Average D is consistent
with solid-state diffusion, at
960 K



Conclusions

- TEM-EDS and SIMS methodologies allow spatial tracking of marker layers in reactive multilayers
- Resolution
 - TEM-EDS: spatial: nm, concentration: 0.1%
 - SIMS: spatial?, concentration: ppm
- Hf marker layers showed atomic diffusion much greater than expected
 - 100's of nm vs. 1's of nm
 - Most likely occurred during elevated temperatures, post-reaction
- Will investigate rapidly quenched materials and unstable fronts

Acknowledgements

- Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.
- Questions?