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

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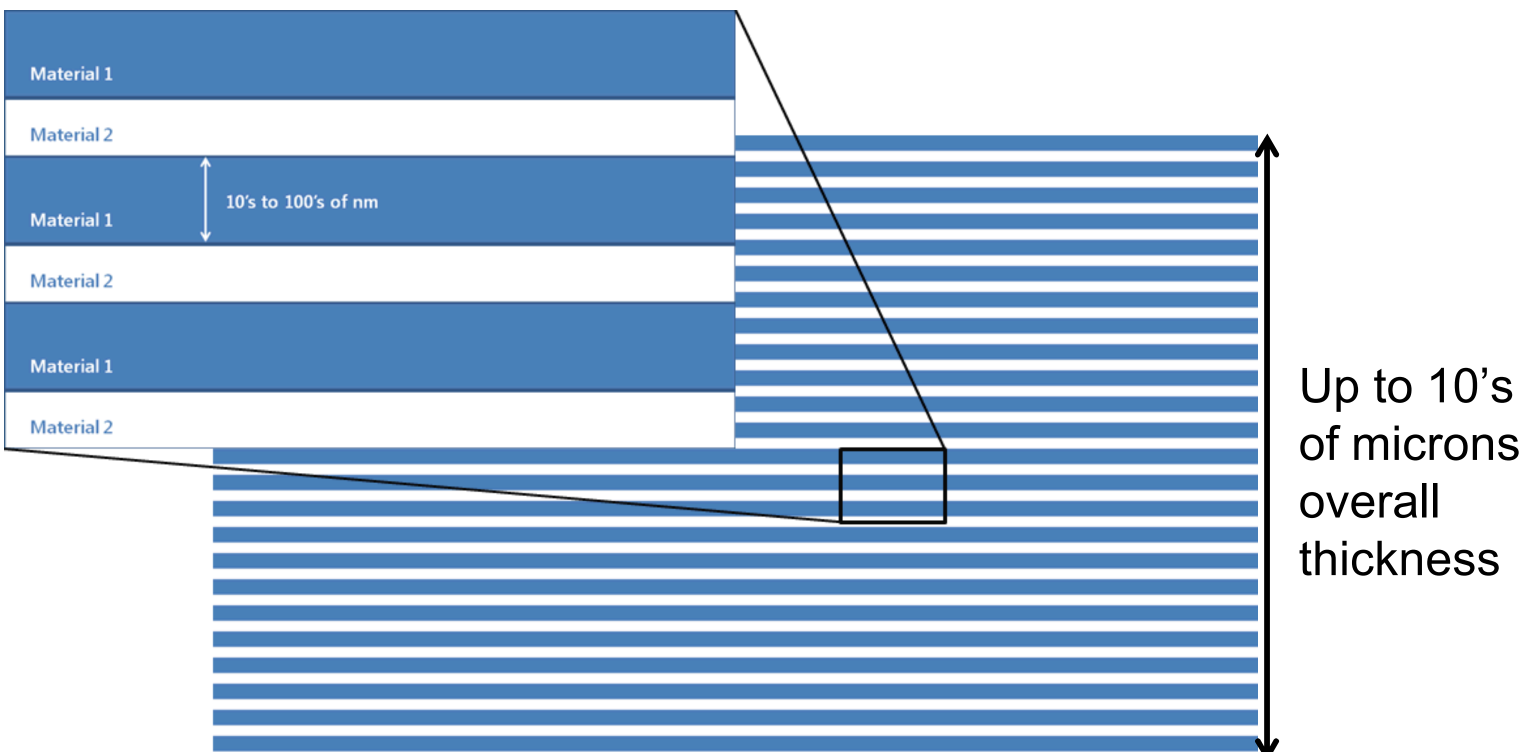
Experimental Material
Zr/2Al Nanolaminates

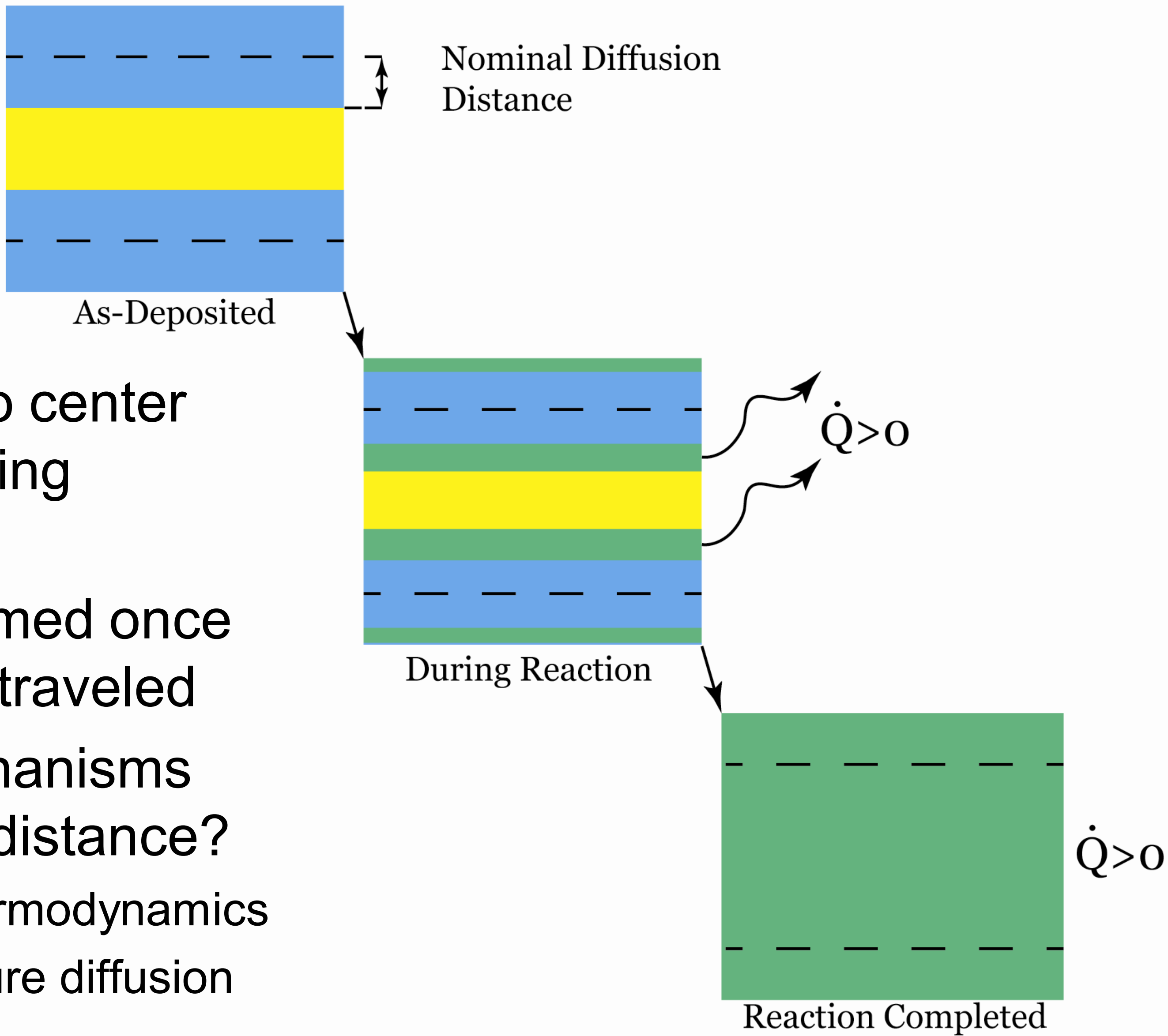
- $Zr + 2Al \rightarrow ZrAl_2; \Delta H_{exp} = -46 \frac{kJ}{mol_{atoms}}$

  (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



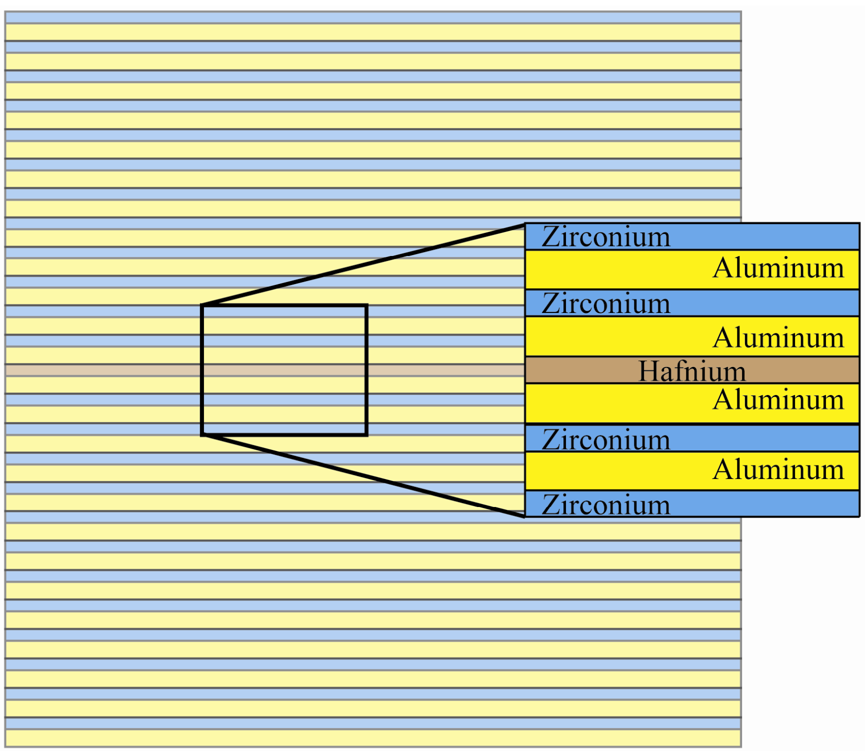
- Atoms diffuse to center line of neighboring reactant layer
- Final phase formed once this distance is traveled
- Can other mechanisms affect diffusion distance?
  - Dissipative thermodynamics
  - High temperature diffusion

Marker Layer Design

Zr+(Hf)/2Al Nanolaminates

Compare ph
properties
DSC results

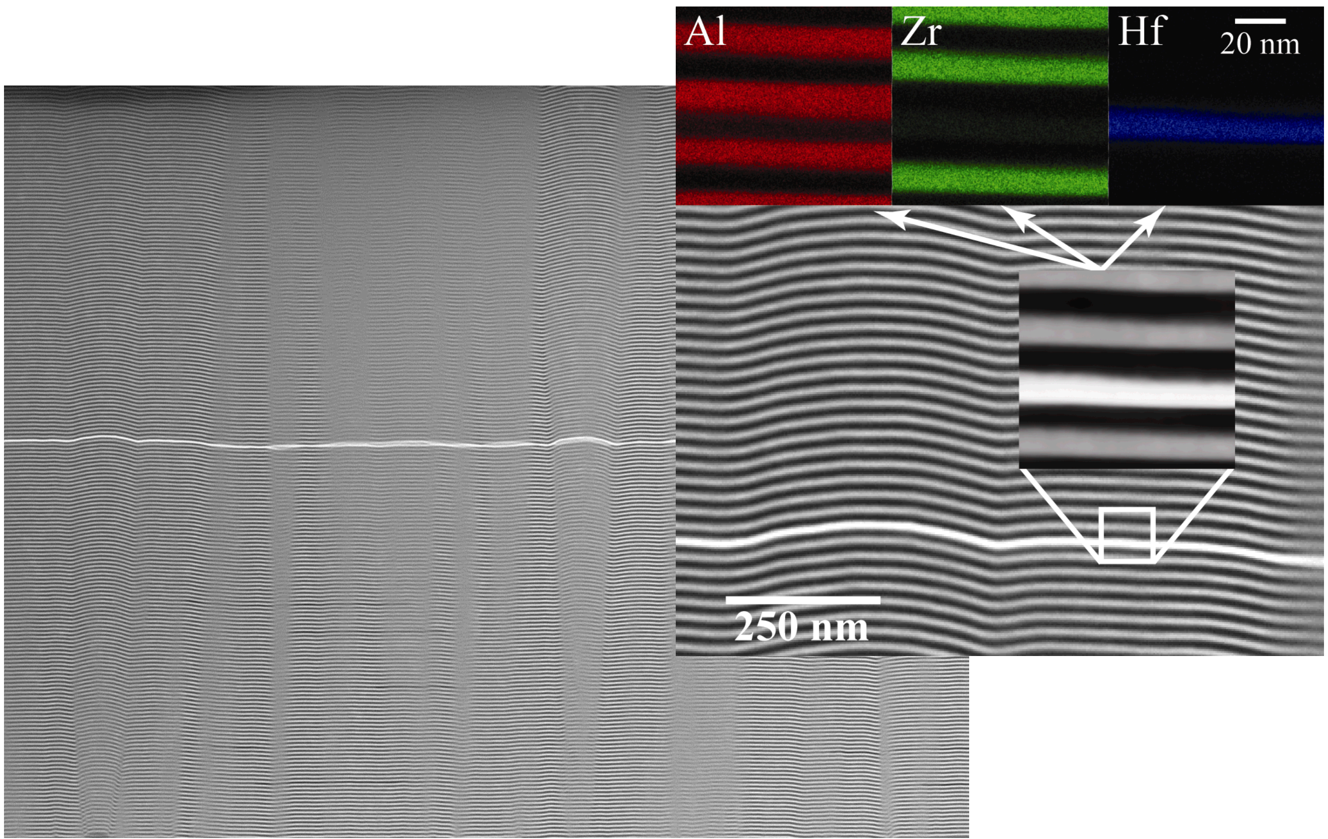
- Hafnium replaces Zr at a single layer
- Hafnium and Zr are miscible with no distinct intermetallic phases
- Similar chemistry and product phases with Al



$ZrAl_2$	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_2Al_3	$T_m \approx$ 1590 °C	Hf_2Al_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

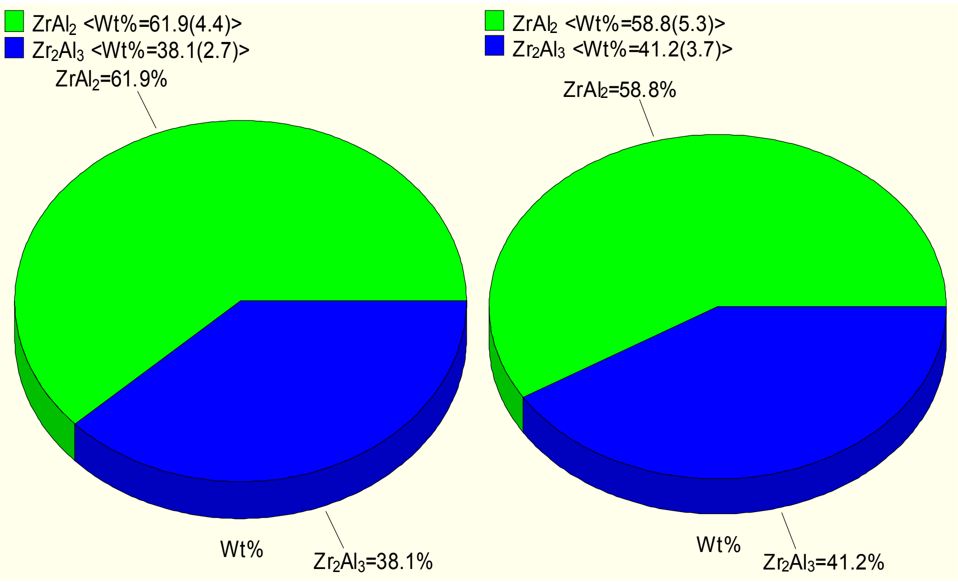
- Marker layer distinct
- Clearly resolvable with z-contrast and EDS in TEM

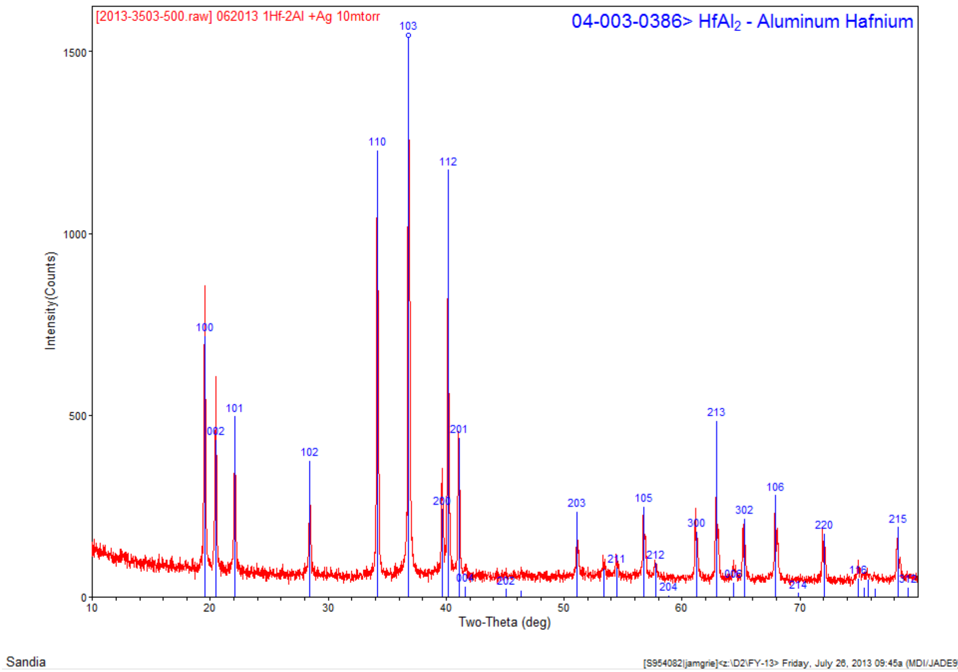


Phase Identification
Zr/2Al and Hf/2Al Standards

- Zr/2Al films reacted in vacuum (10 mTorr)
- $ZrAl_2$ (~60% wt%) and Zr_2Al_3 (~40% wt%) phases identified by XRD

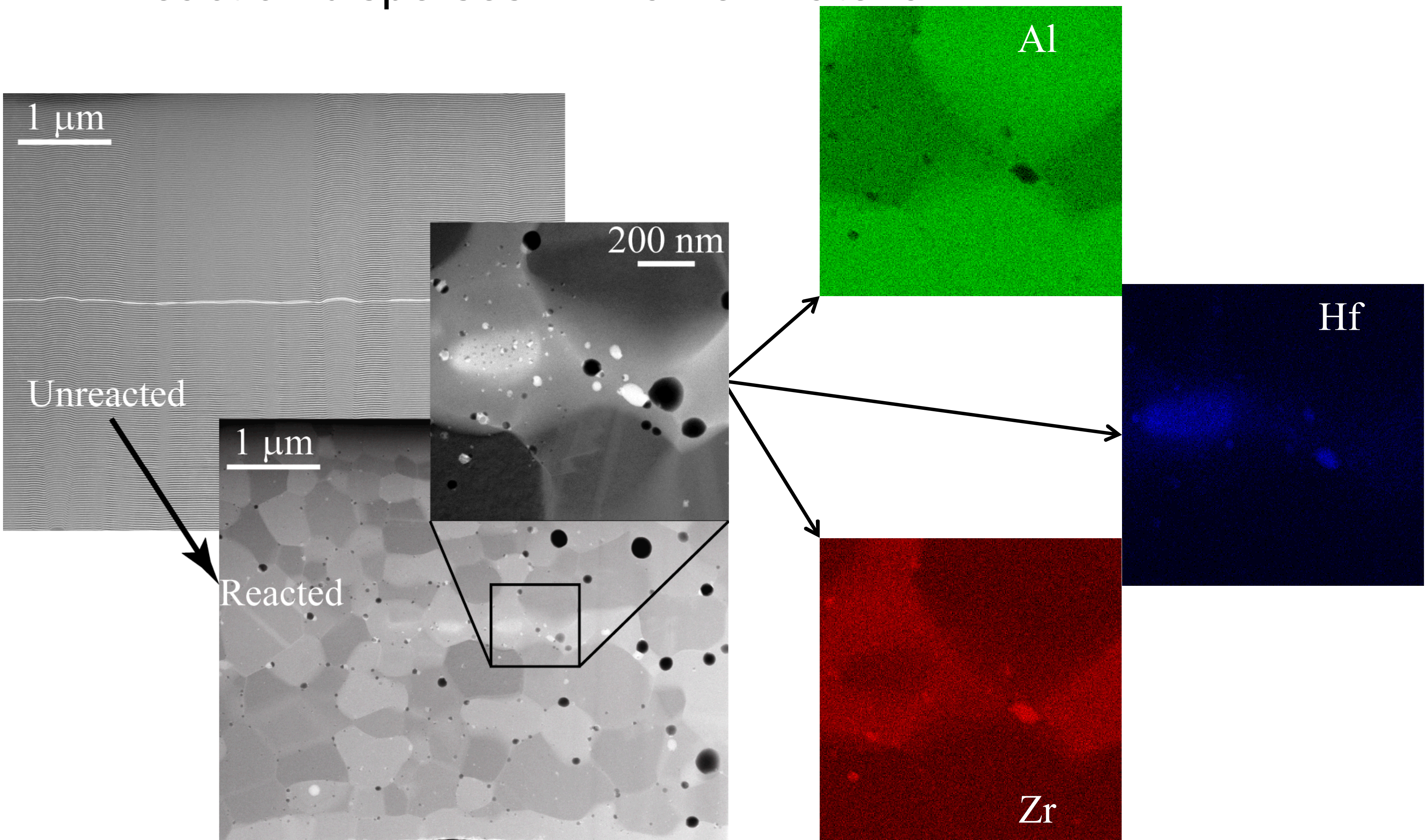
- Hf/2Al films reacted in vacuum (10 mTorr)
- Phase pure $HfAl_2$





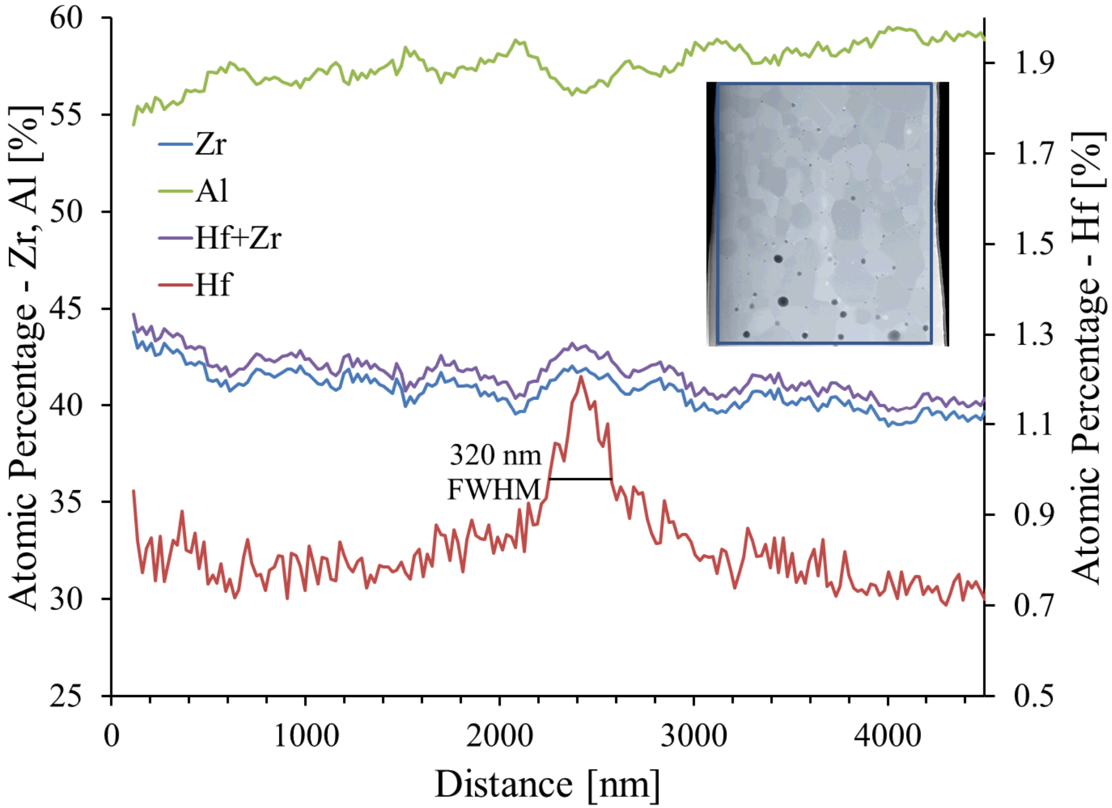
Marker Layer Design
Zr+(Hf)/2Al Nanolaminates

- Reaction disperses Hf marker material

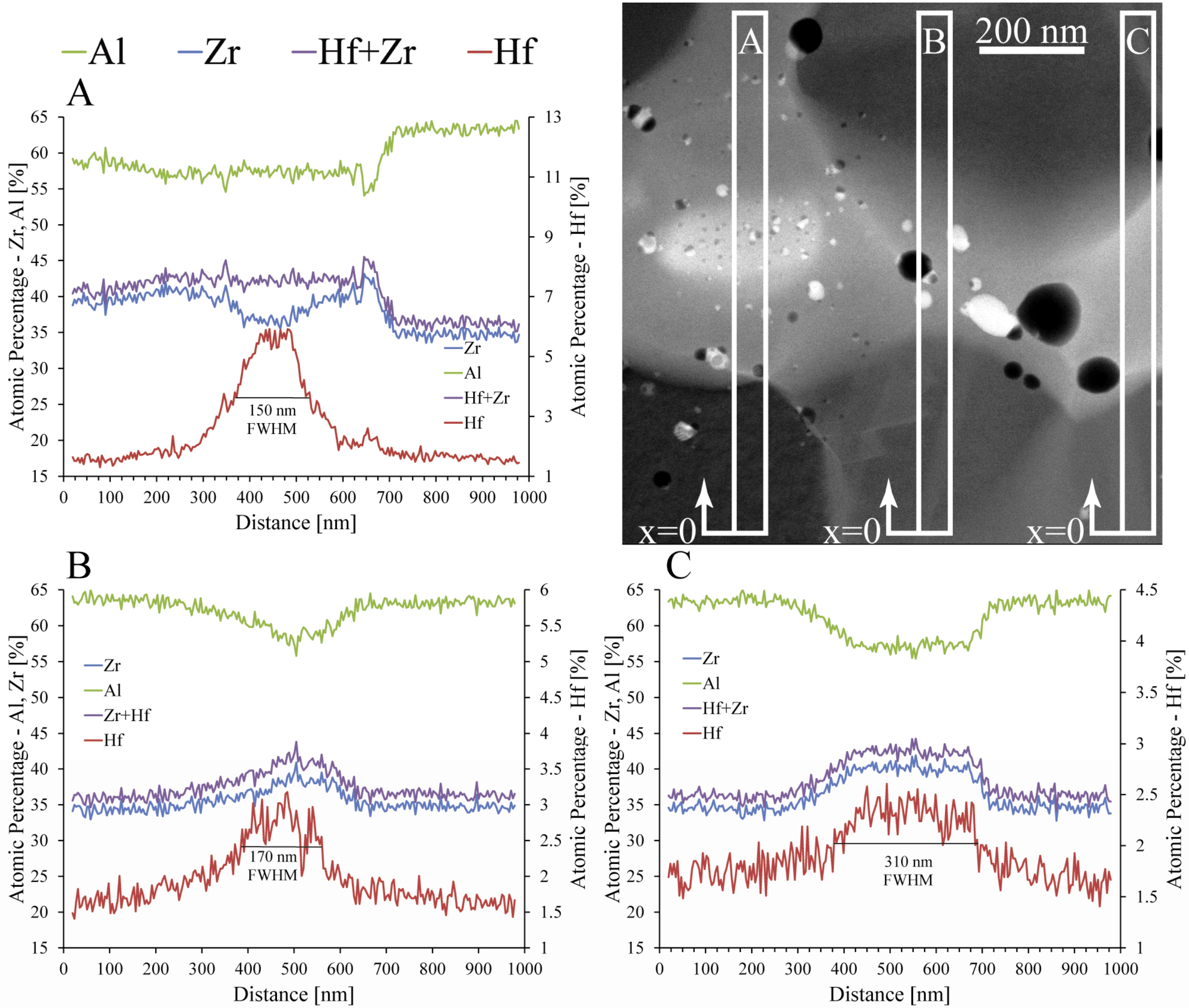


Marker Layer Design
Zr+(Hf)/2Al Nanolaminates

- Reaction disperses Hf marker material
- 14 kx magnification – 5 x 5 μm ROI
- Probed through EDS and SIMS

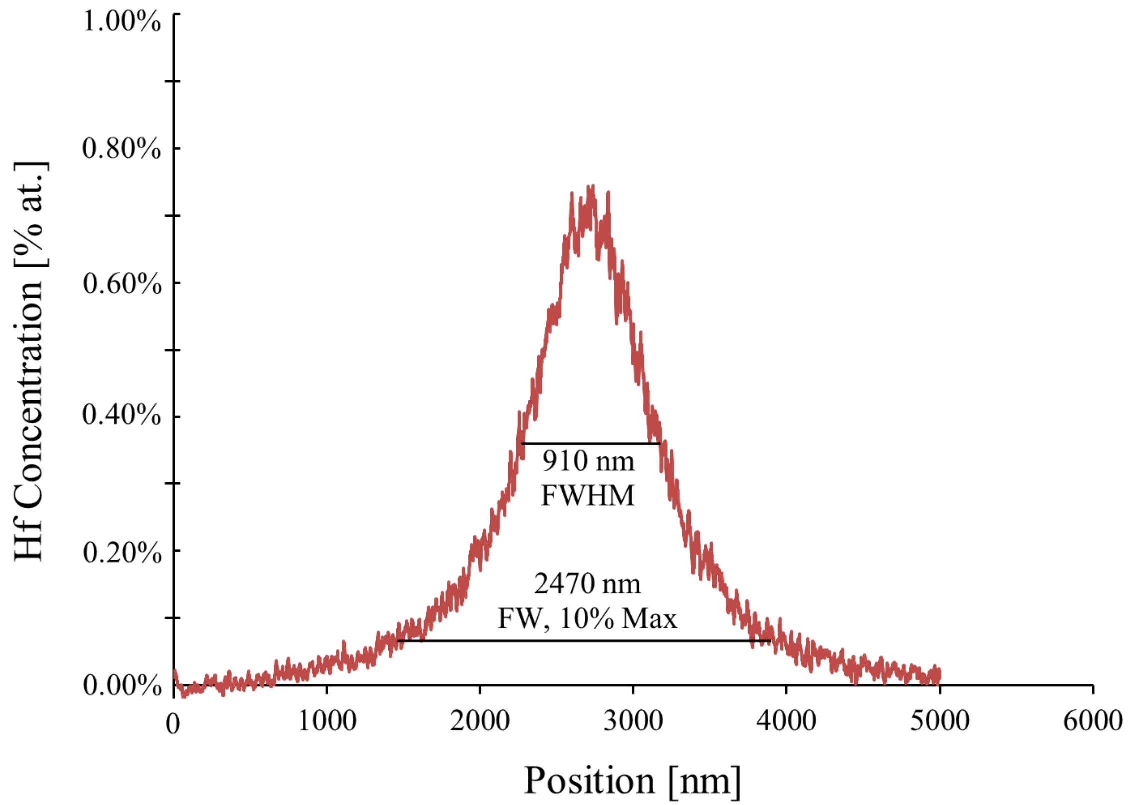


Variation at smaller length scales

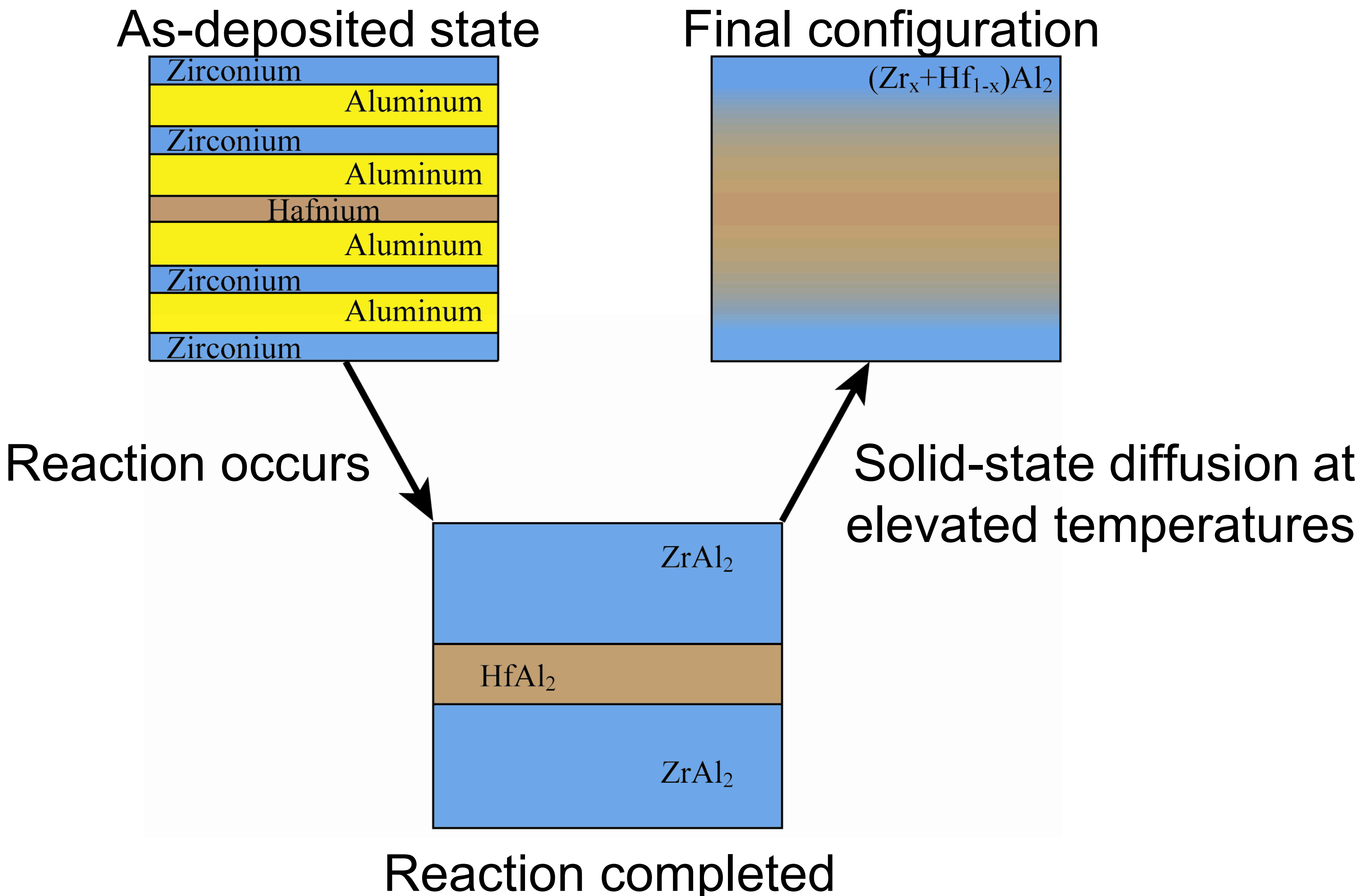


Marker Analysis by SIMS
Zr+(Hf)/2Al Nanolaminates

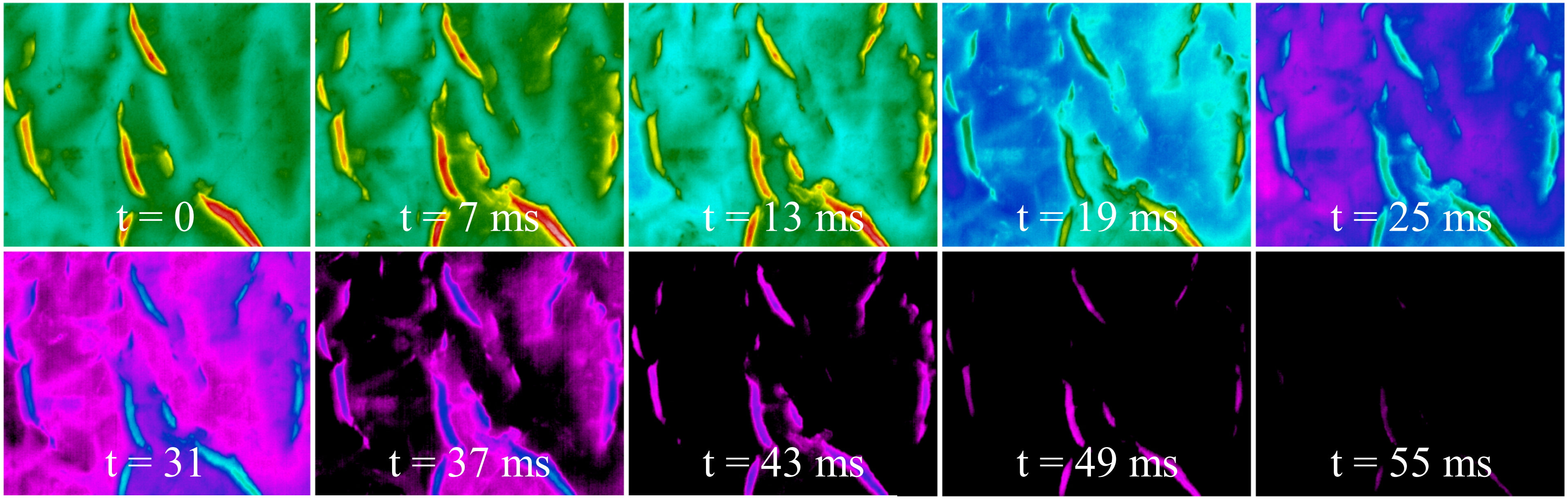
- Sputter area = 200 x 200 μm^2
- Analysis area = 50 x 50 μm^2 – much greater area than EDS
- Hf-baseline subtracted from signal

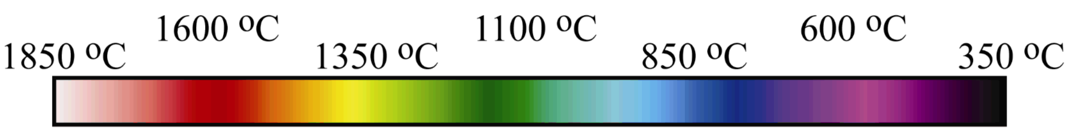


Diffusion model – Assumed progression

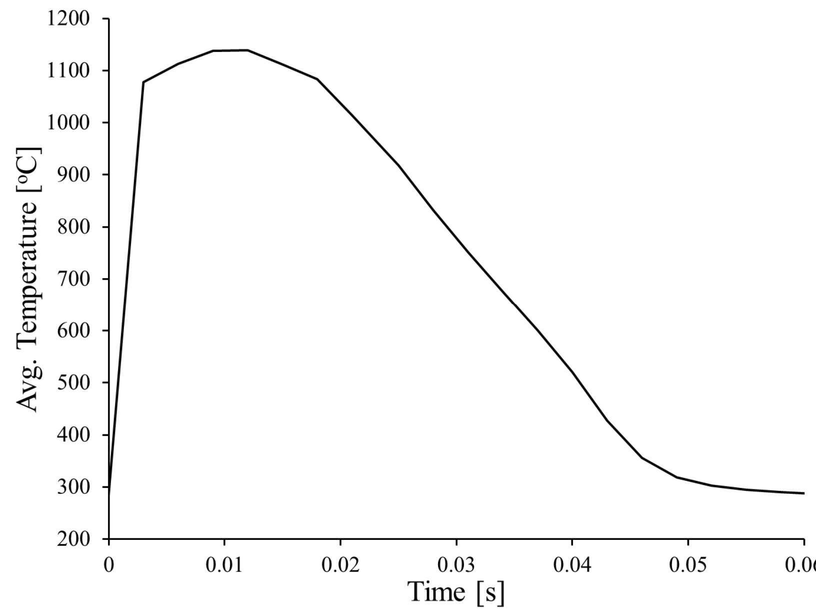


IR imaging of temperature history

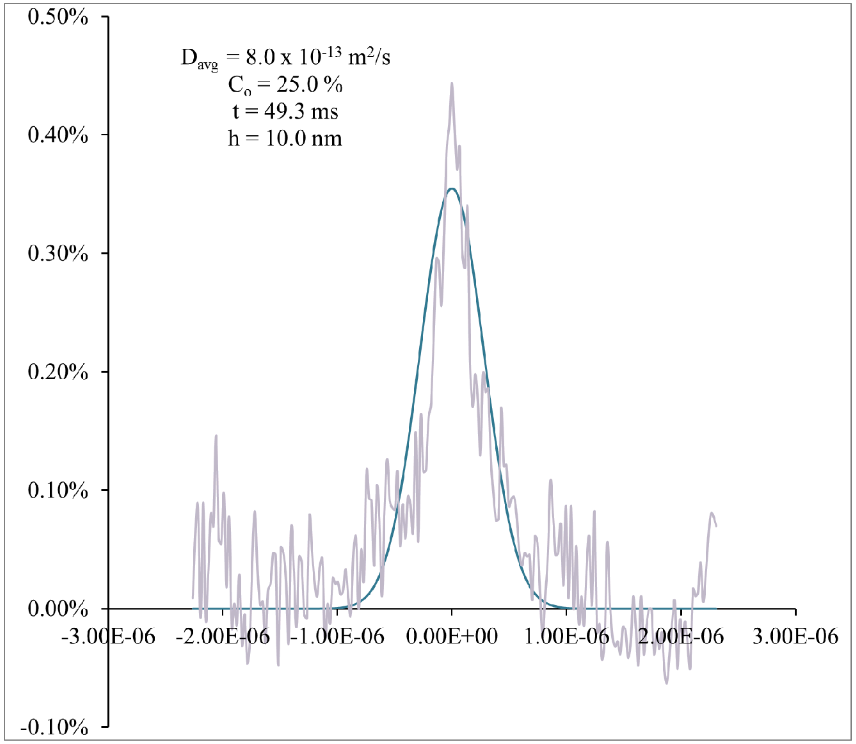




- Plot is average meas. temp of surface in image (4.8 x 3.8 mm)
- Time average over 46 ms is 690 ºC (963 K)
- Information for comparison to best fit results from diffusion model



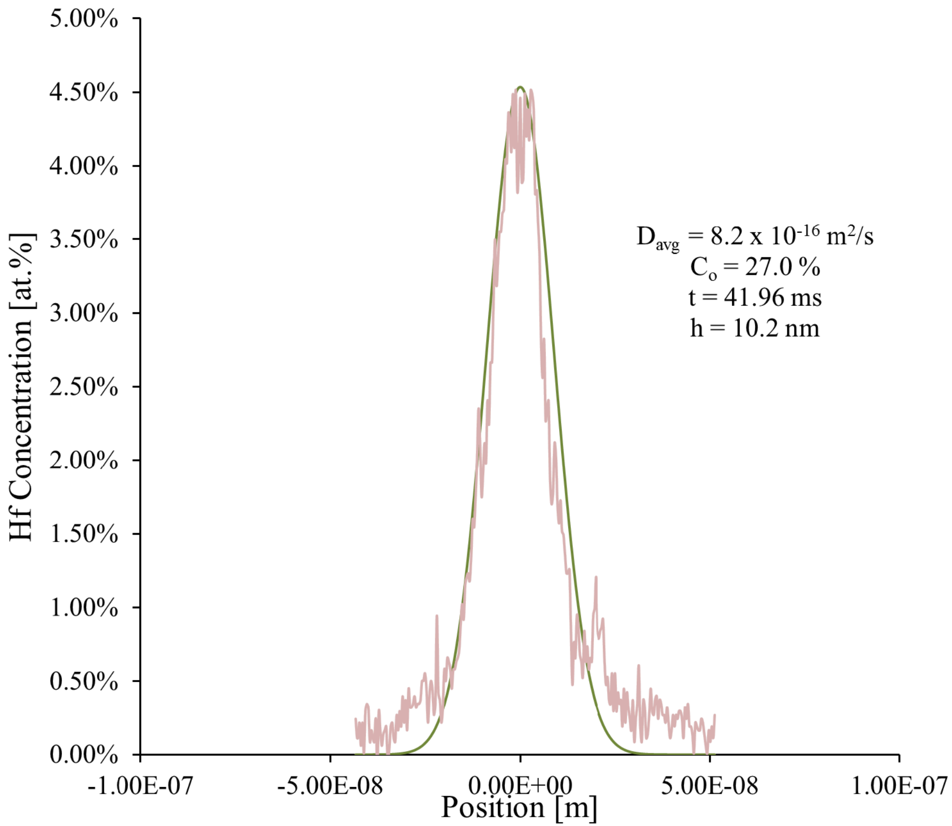
Diffusion model – Compare to EDS data

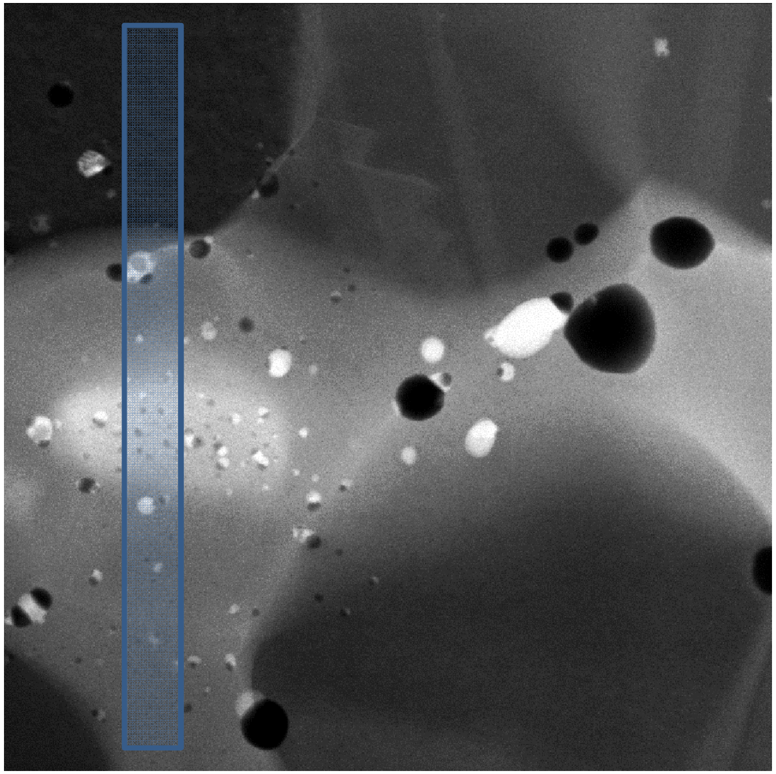


- Integration of EDS Hf signal over full 14 kx image (5x5 μm)
- Fits do not match well with simple diffusion model and assumptions

Diffusion model – Compare to EDS data

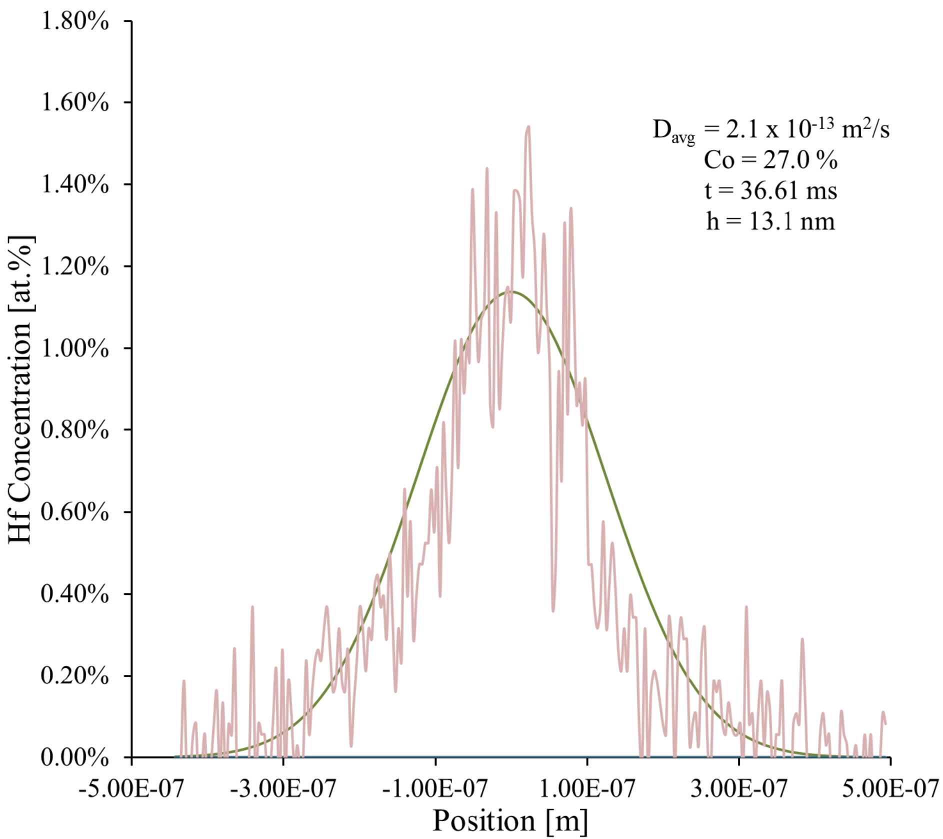
- Integrated profile across 40 nm x 1000 nm path (shown)
- Best fit D = 8.2×10^{-16} m^2/s

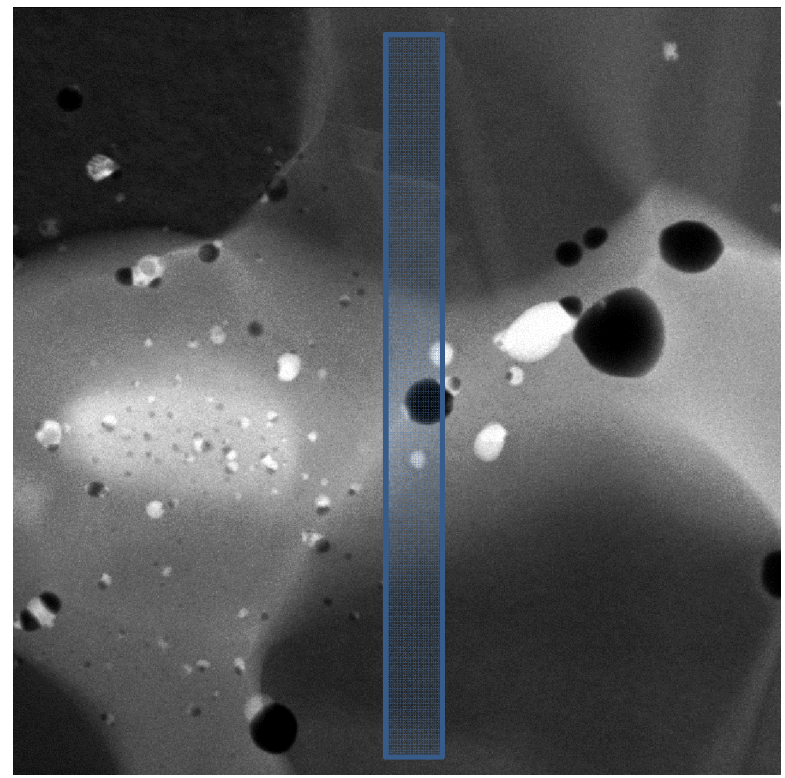




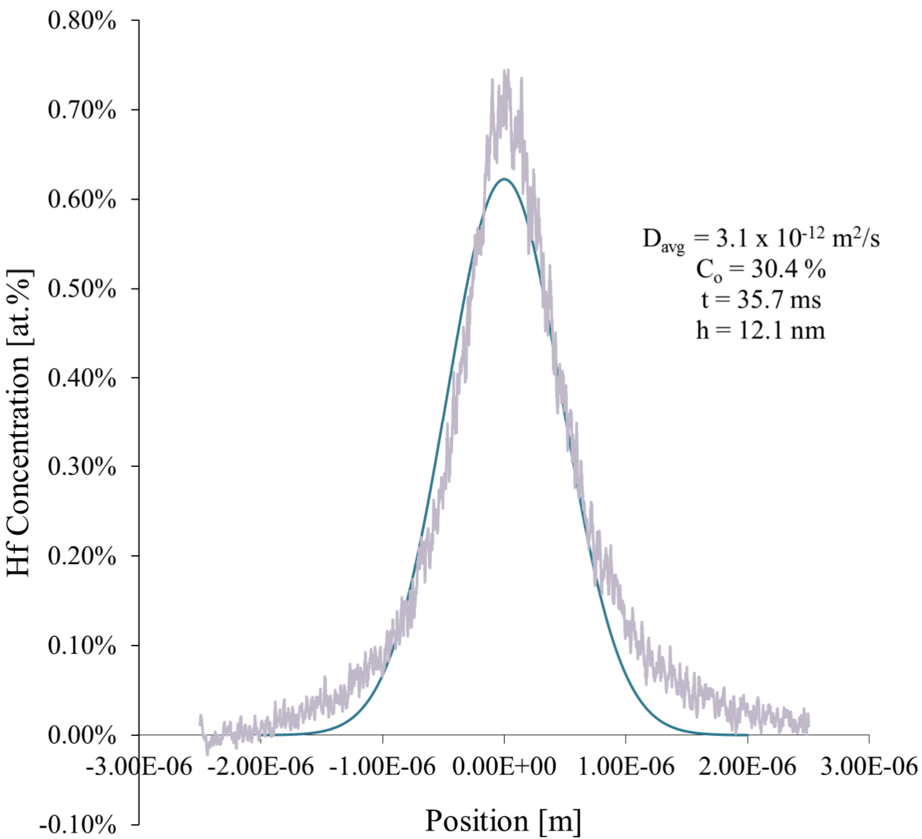
Diffusion model – Compare to EDS data

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





Diffusion model – Compare to SIMS data



- Best fit D = 3.1 x 10^{-12} m^2/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

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- Questions?