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

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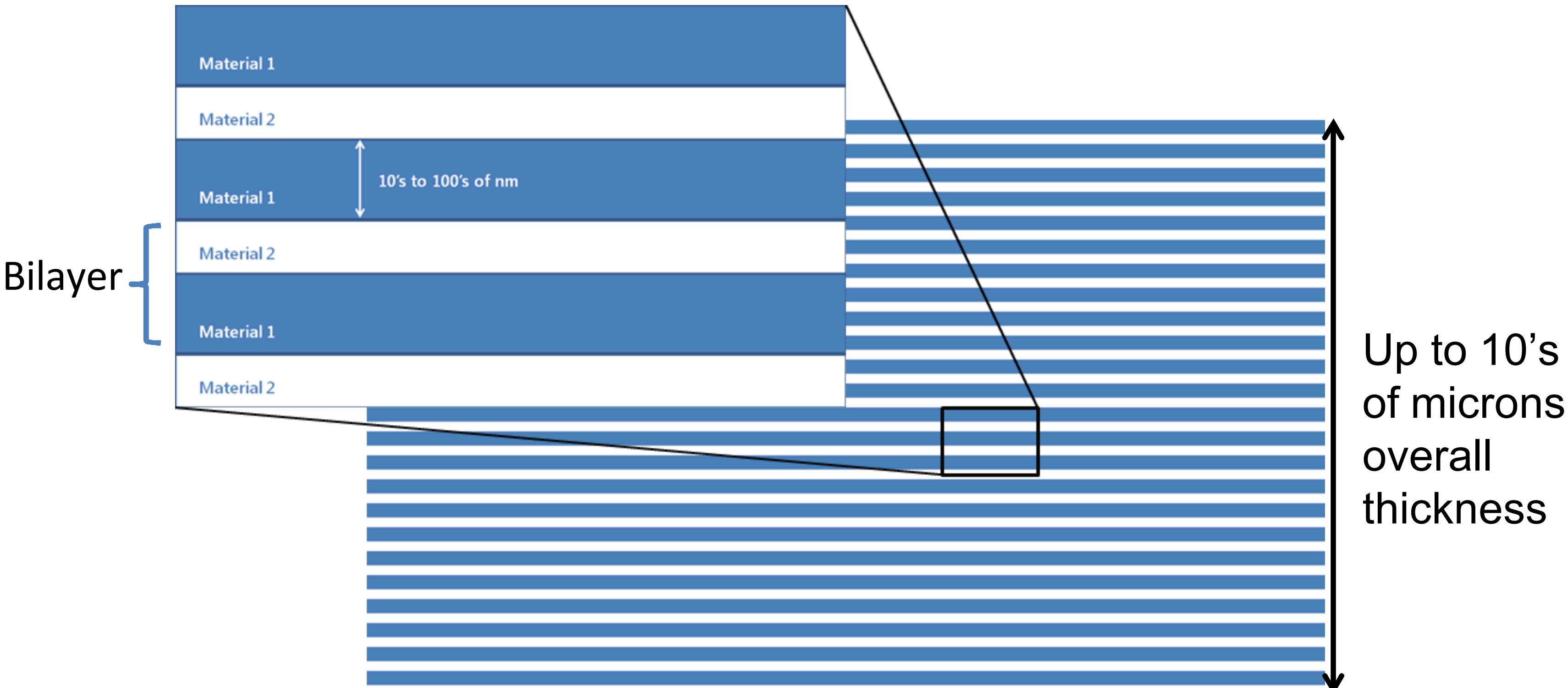
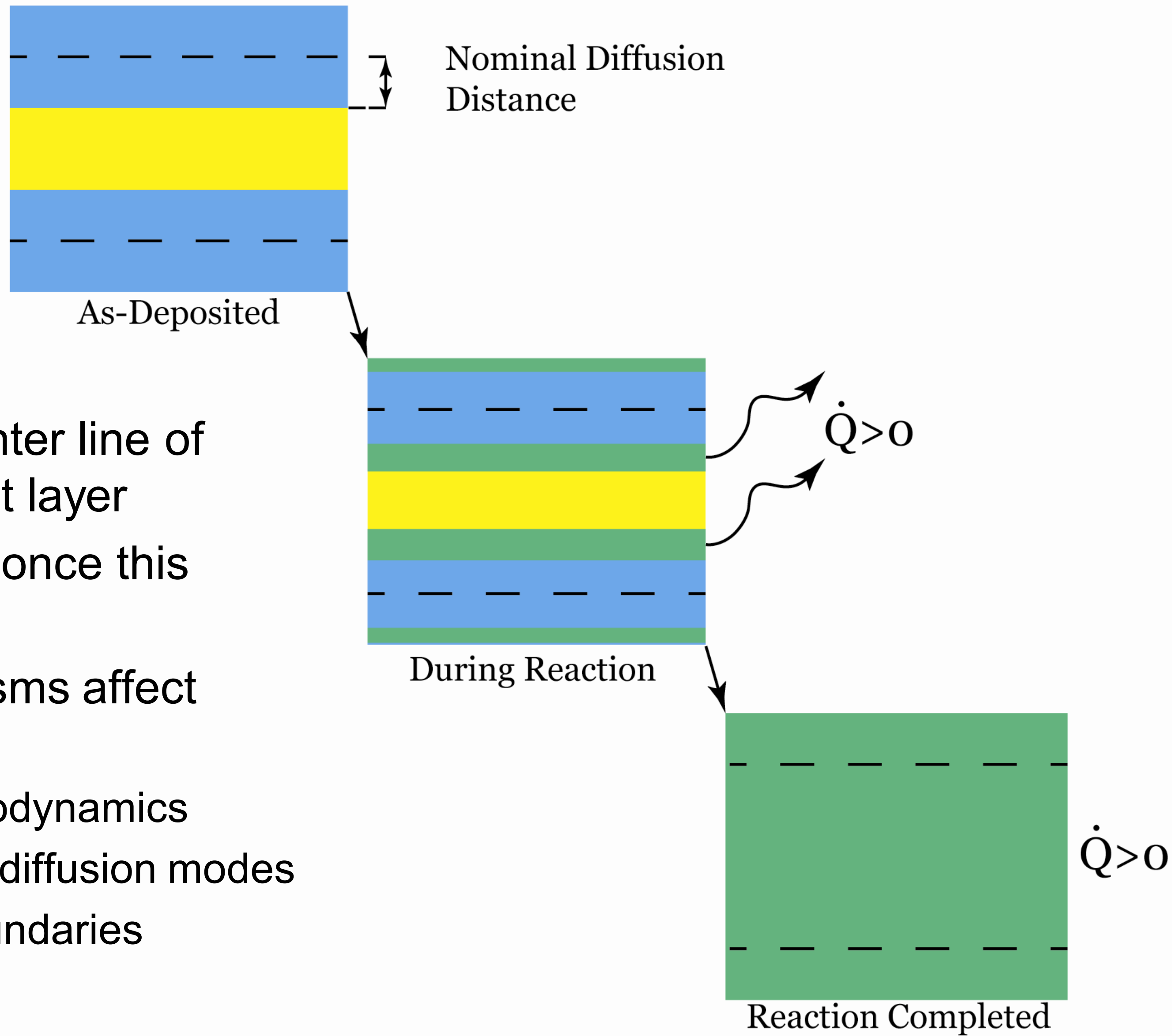
Experimental Material: Zr/2Al

- *Zr + 2Al* $\rightarrow$ *$ZrAl_2$; ΔH_{exp} = -46 kJ/mol atoms*
  (de Boer, Cohesion in Metals)

- Typical design of sputtered reaction foils:
  single bilayer per foil, total thickness = 5.0 μm
  sputter deposited (pure) metals, full density



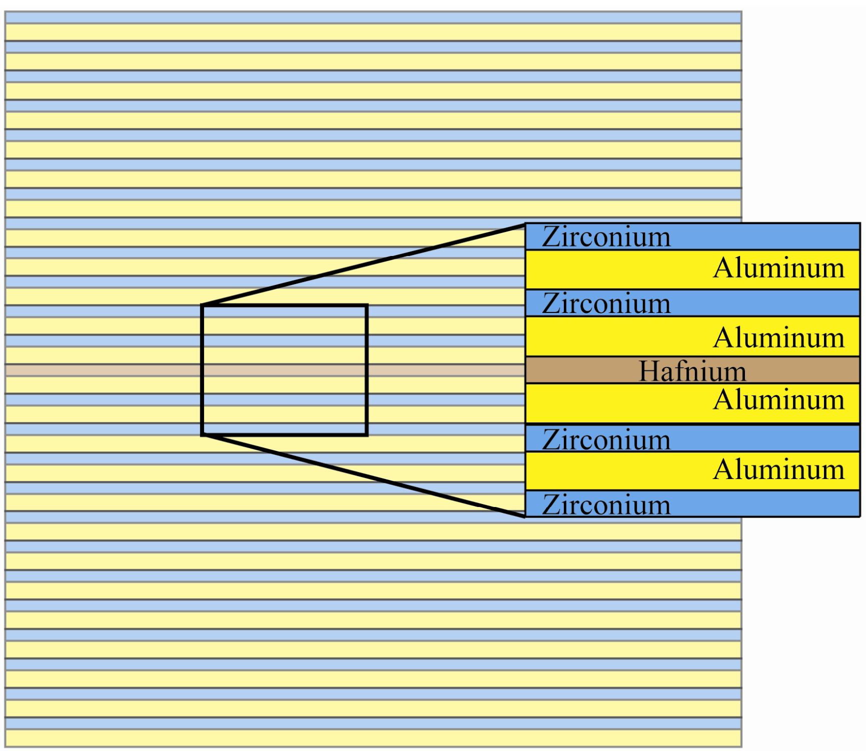
Nanolaminates
Assumed Reaction Progression



- 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 modes
  - Defects, grain boundaries

Marker Layer Design
Zr/2Al Nanolaminates with one Hf layer

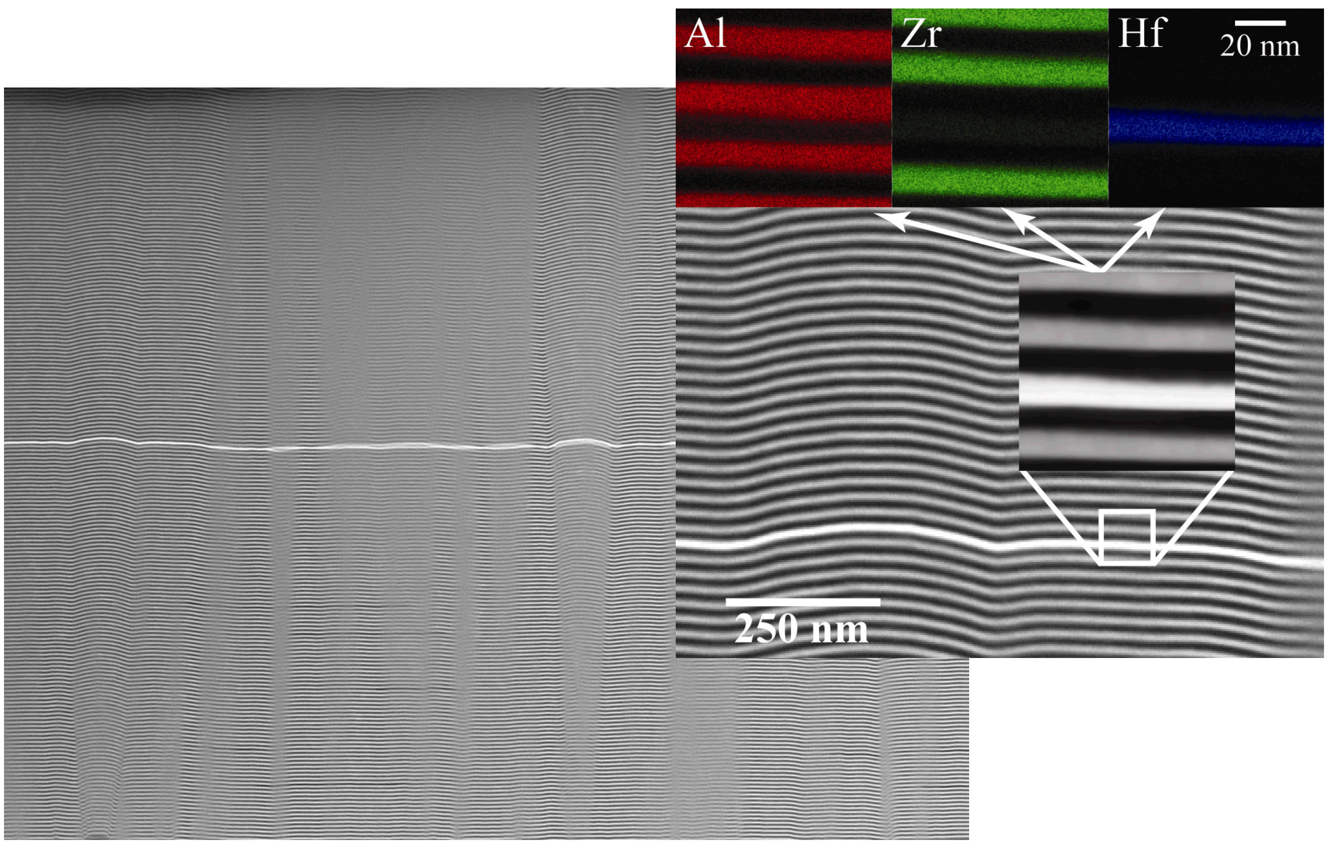
- Hafnium replaces Zr at a single layer
- Hafnium and Zr are miscible with no distinct intermetallic phases
- Similar product phases with Al
- Similar chemistry for Zr and Hf, due to lanthanide contraction



$ZrAl_2$	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 ≈ 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 Revealed
Zr/2Al Nanolaminates with one Hf layer

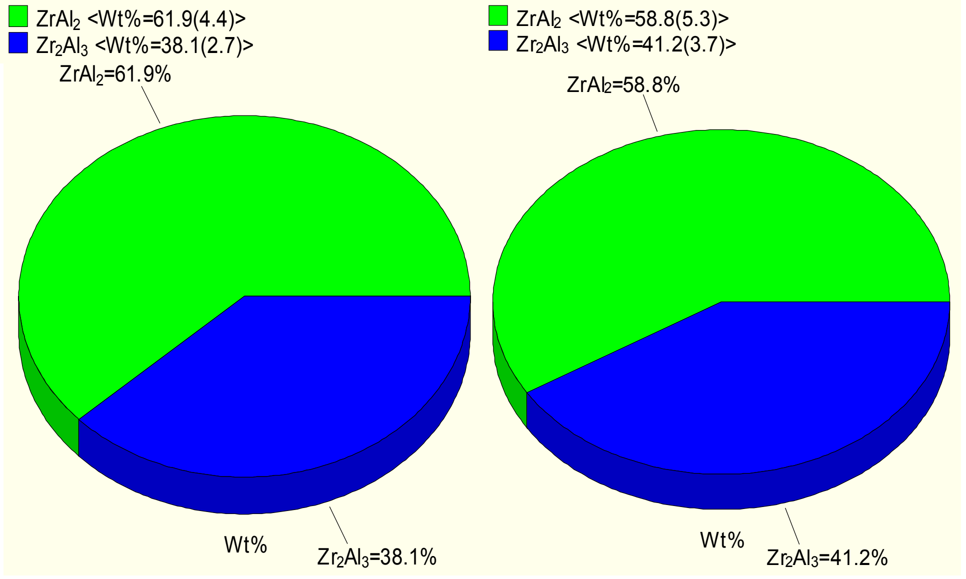
- Marker layer distinct
- Hf placed at center of multilayer
- Clearly resolvable with z-contrast and EDS in TEM

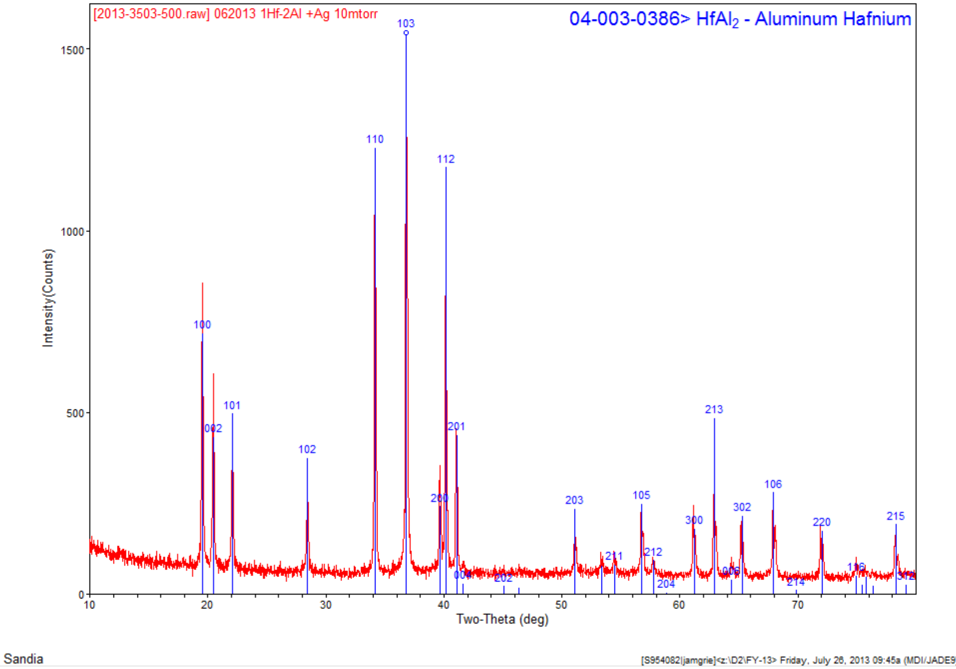


Phase Identification
Zr/2Al and Hf/2Al Standards

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

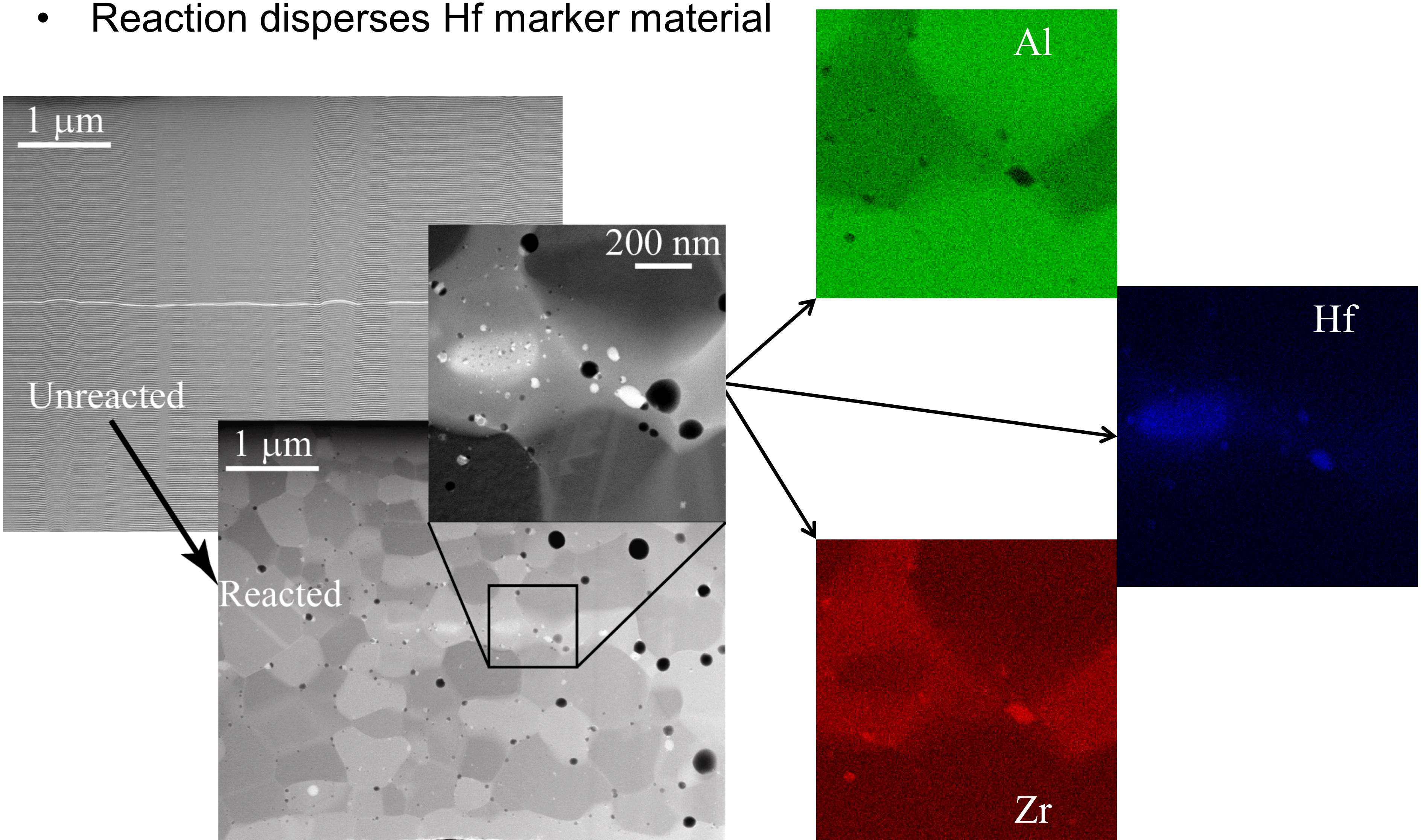
- Hf/2Al films reacted in vacuum (10mT)
- Phase pure $HfAl_2$





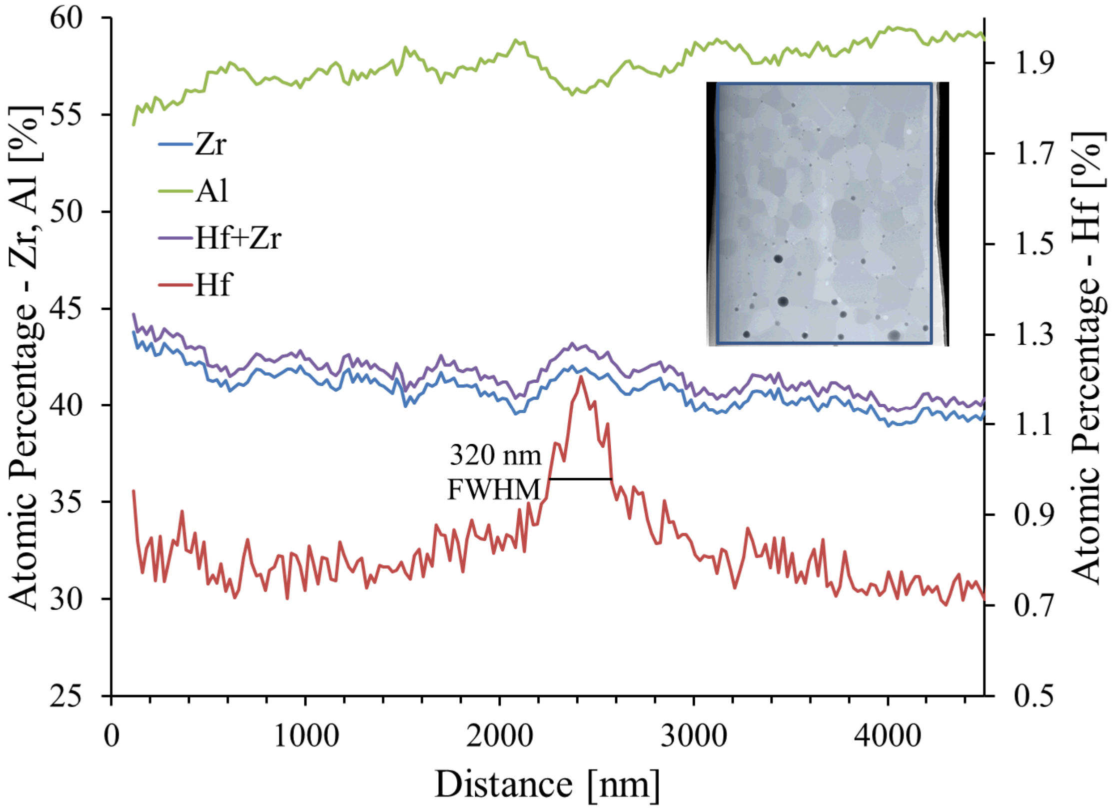
Marker Layer Design
Zr+(Hf)/2Al Nanolaminates

- Reaction disperses Hf marker material

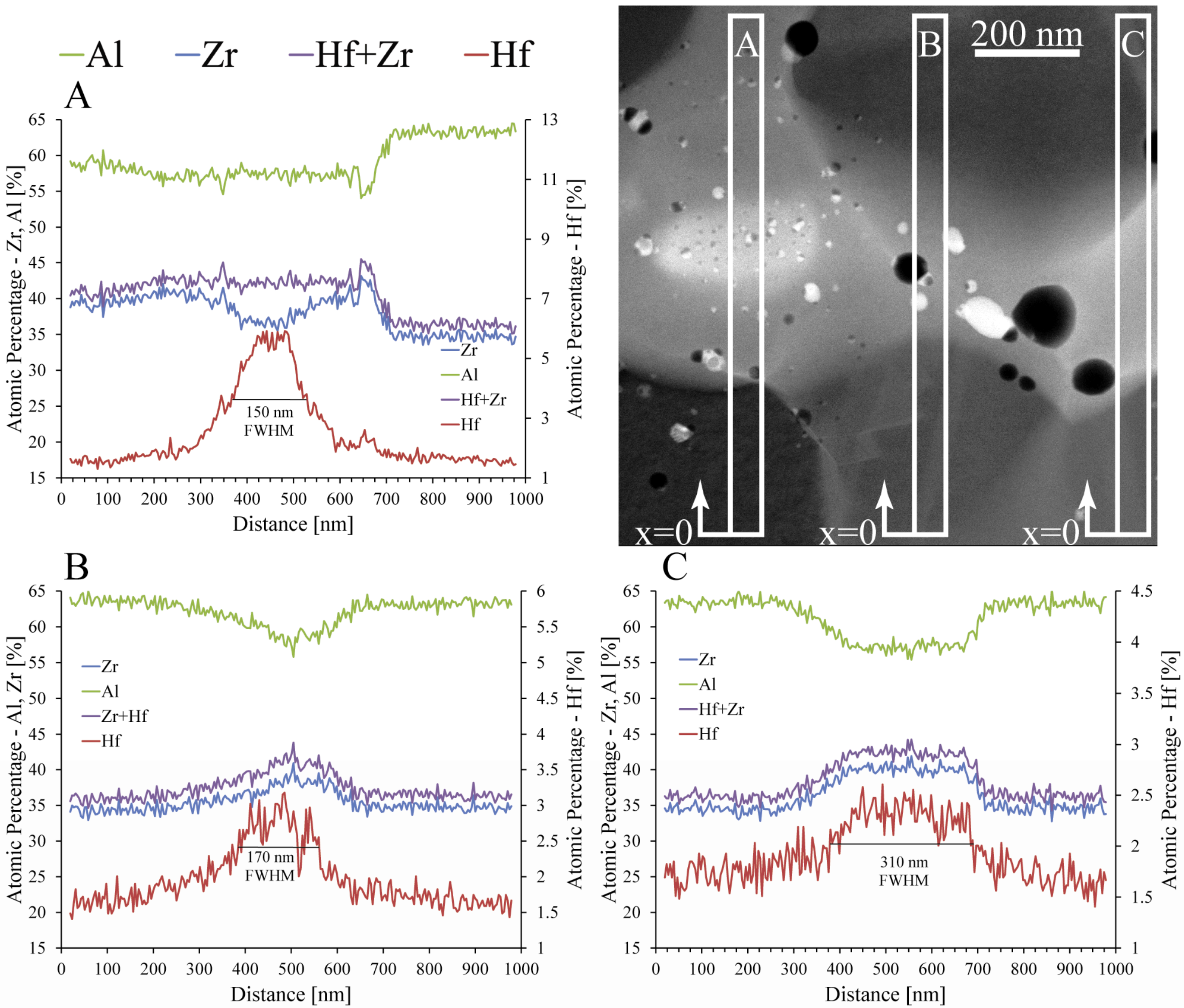


Marker Layer Design
Zr+(Hf)/2Al Nanolaminates

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

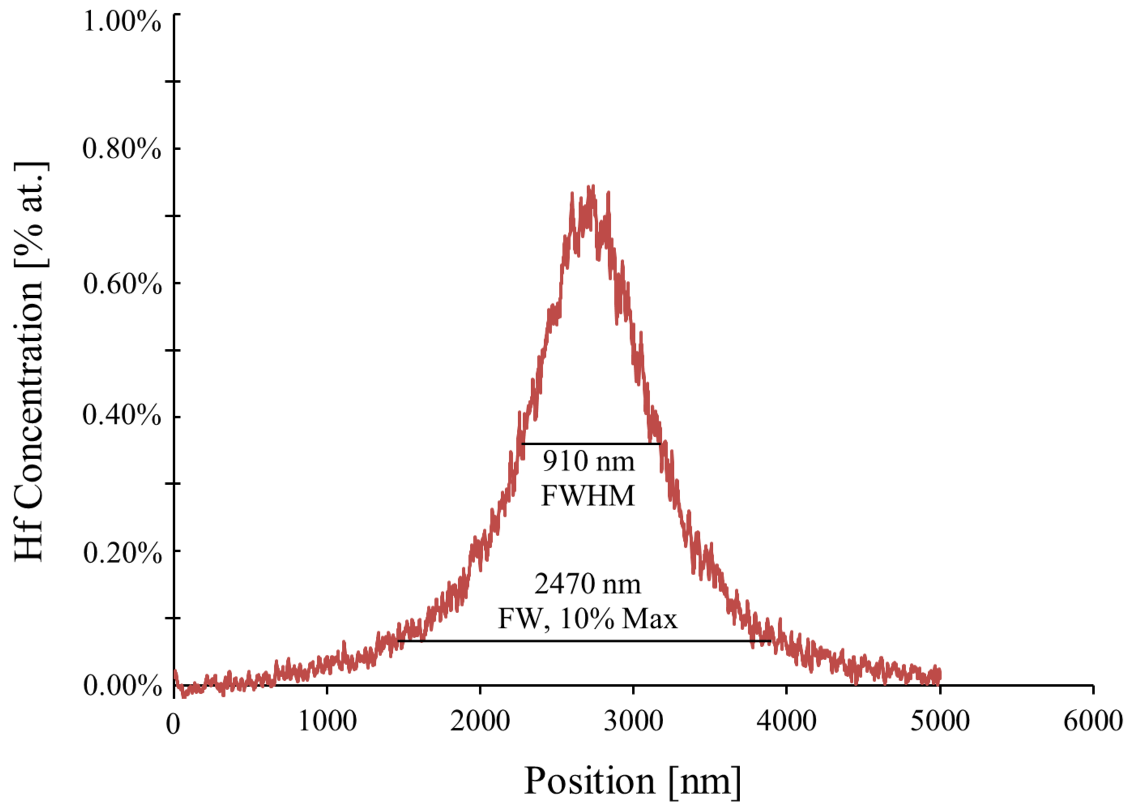


Variation at smaller length scales

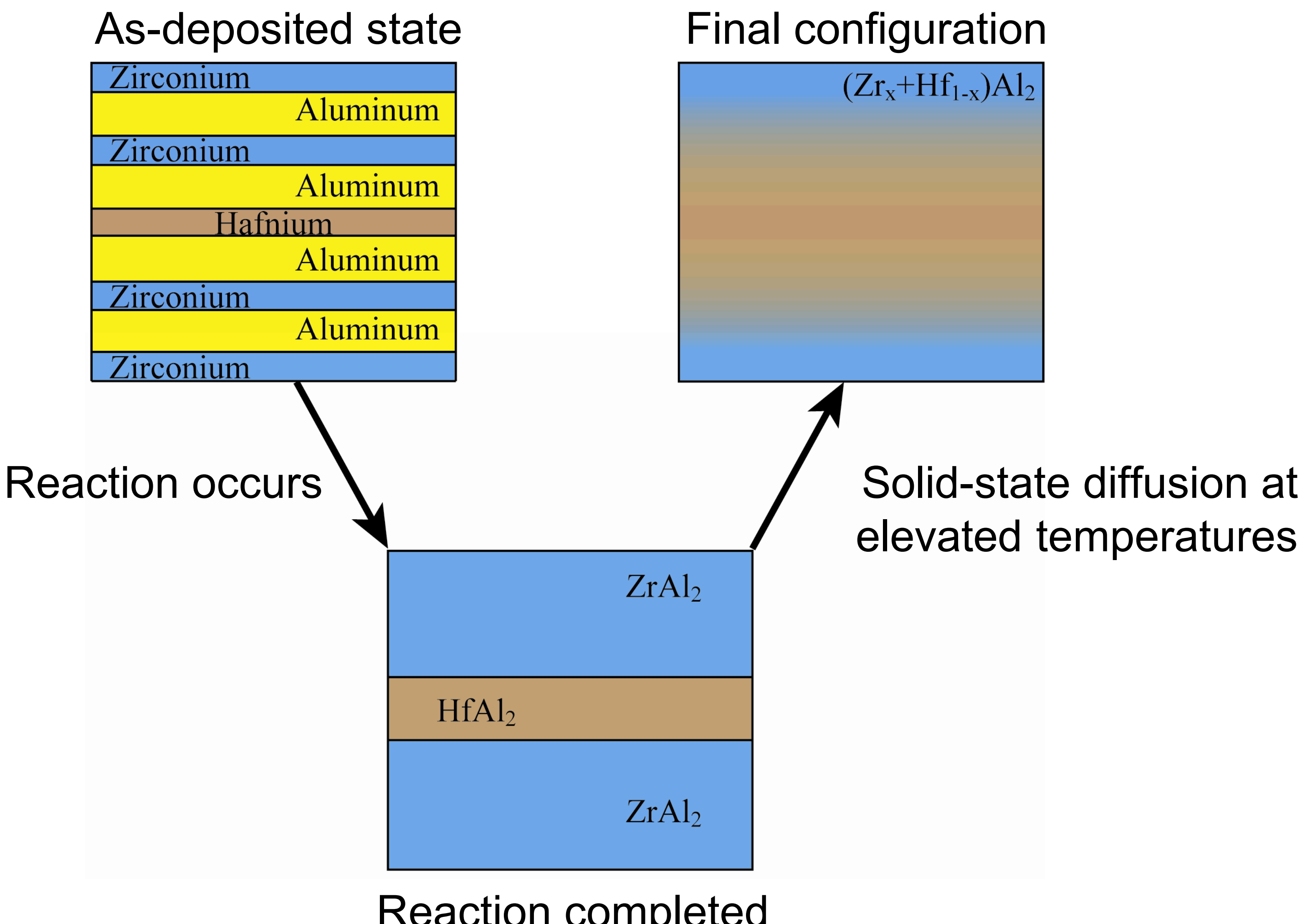


Marker Analysis by SIMS
Zr+(Hf)/2Al Nanolaminates

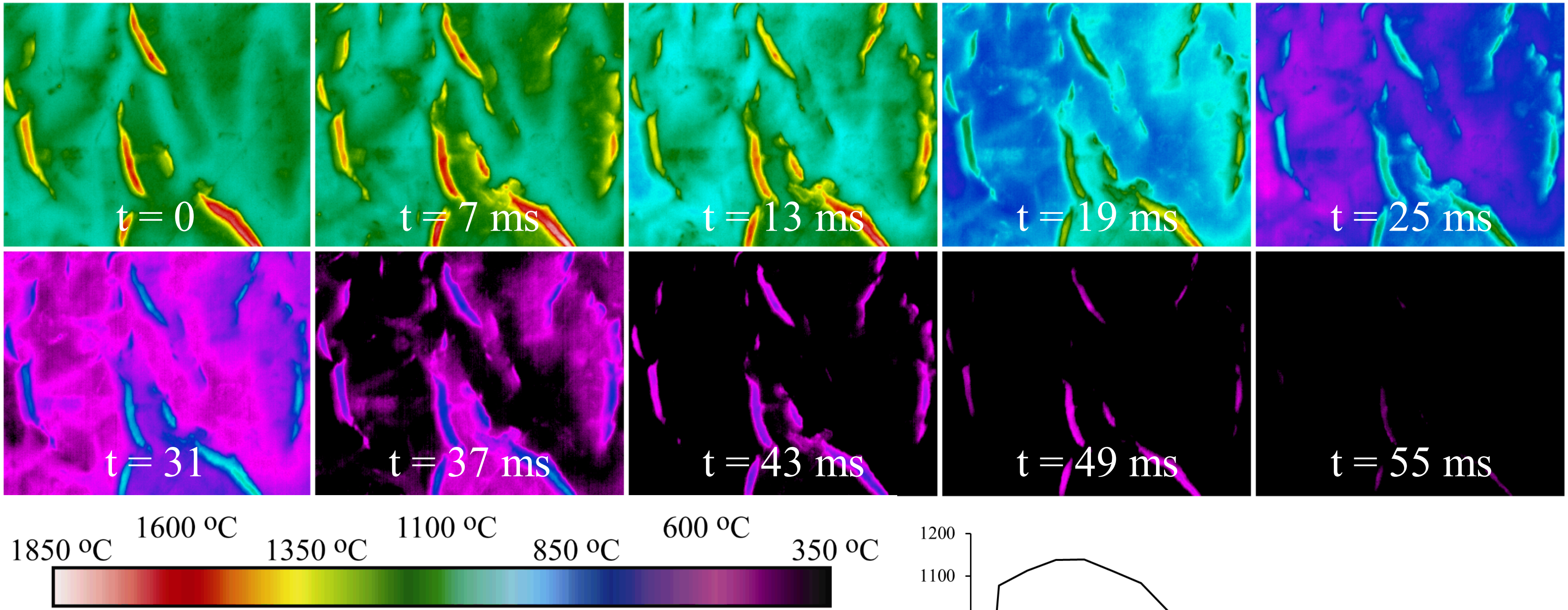
- Sputter area = 200 x 200 μm^2
- Analysis area = 50 x 50 μm^2 – much greater area than EDS
- Hf-baseline subtracted from signal



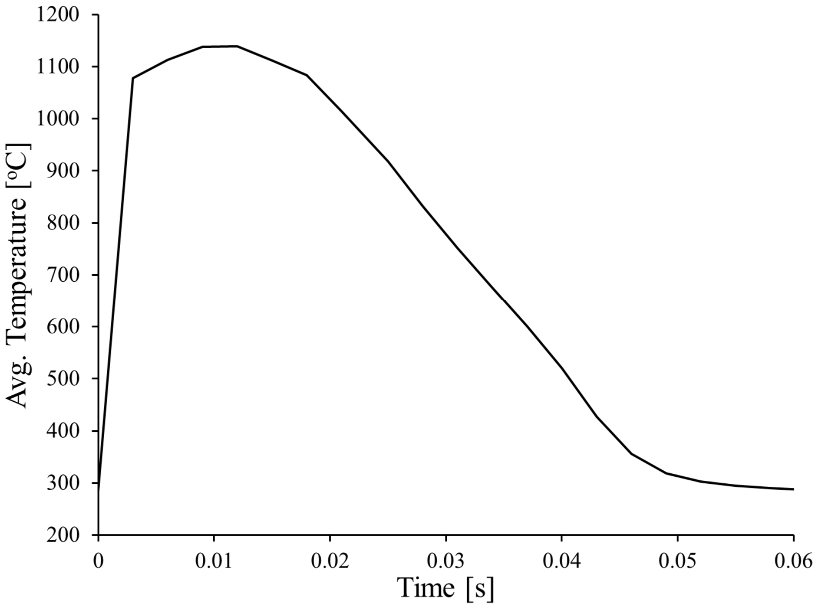
Diffusion model – Assumed progression



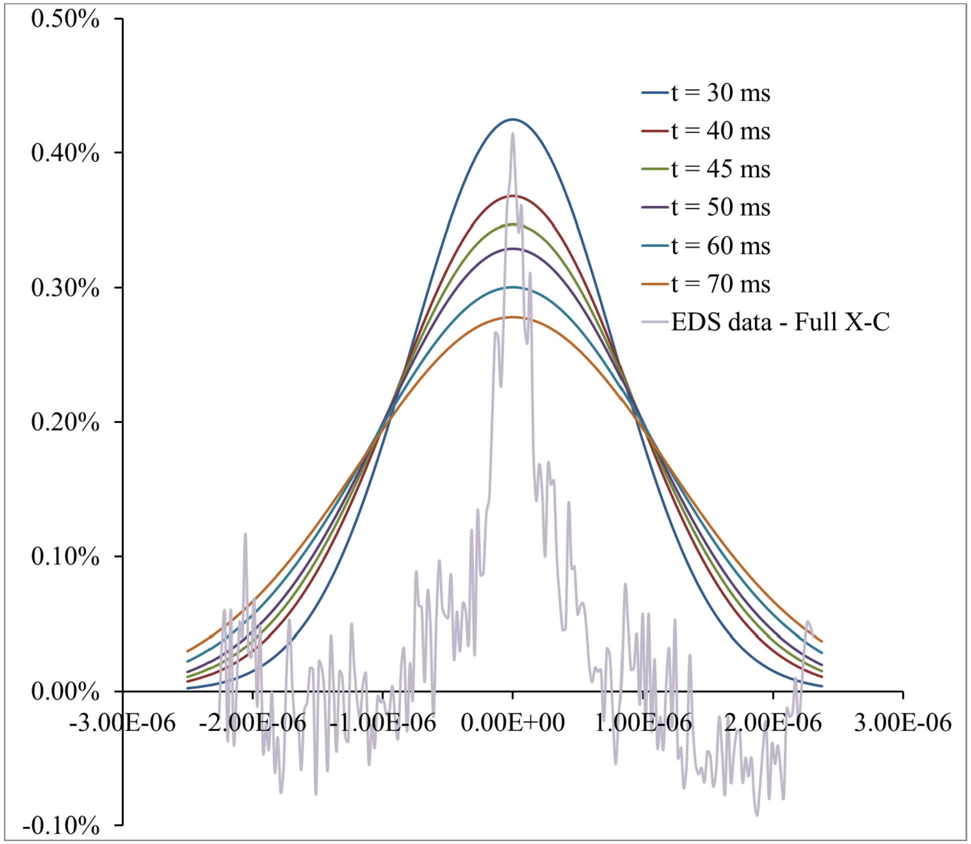
IR imaging of temperature history



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



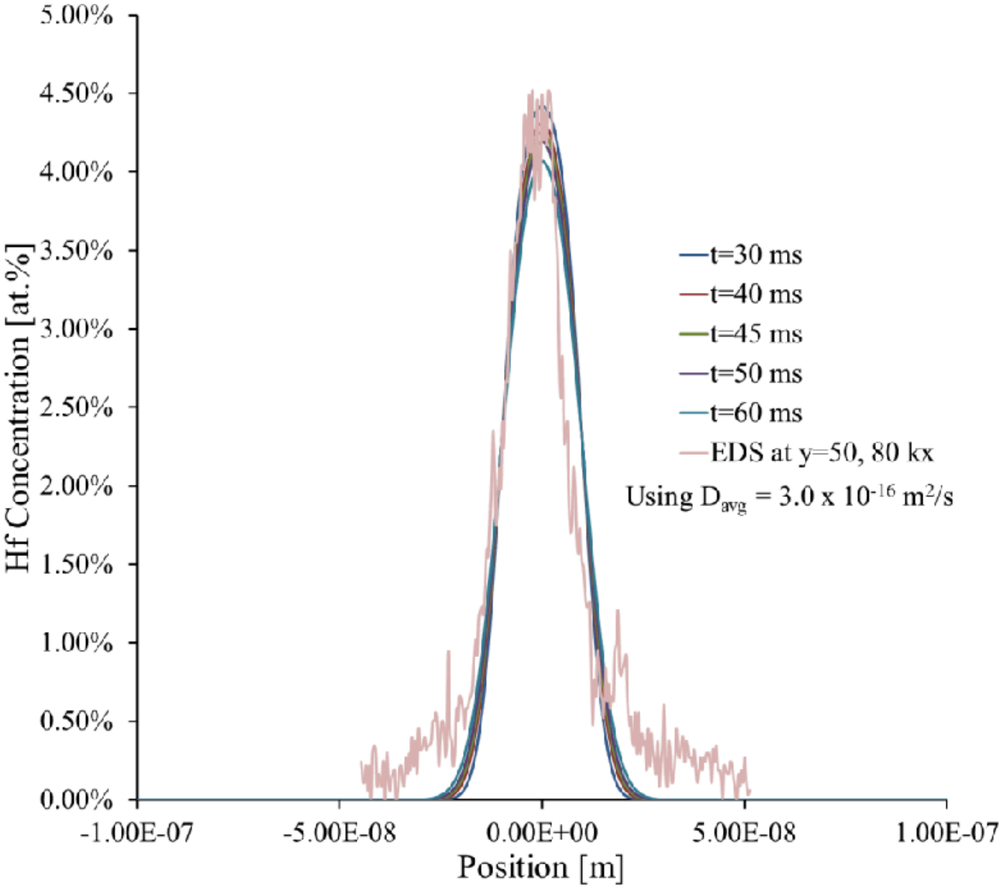
Diffusion model



- Integration of EDS Hf signal over full 14 kx image (5x5 μm)
- Average D is consistent with solid-state diffusion

50 nmBL

Diffusion model

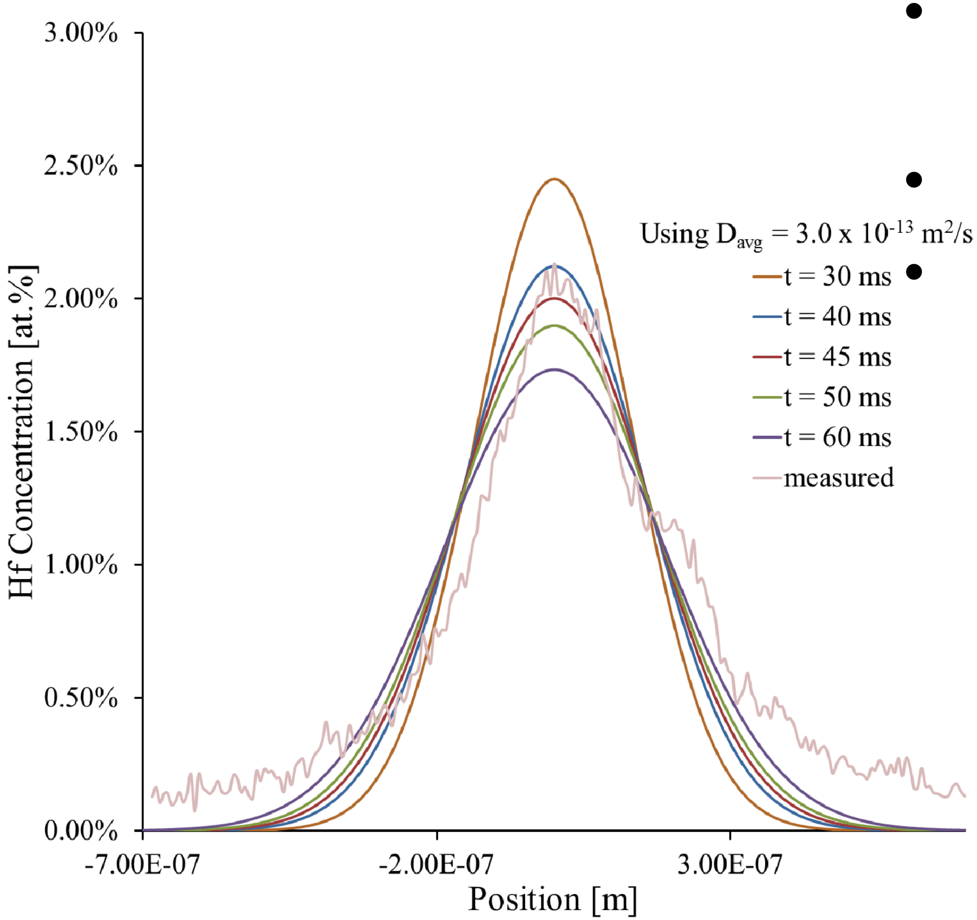


Integrated profile across 40 nm path at location shown, y=50

80 kx, EDS

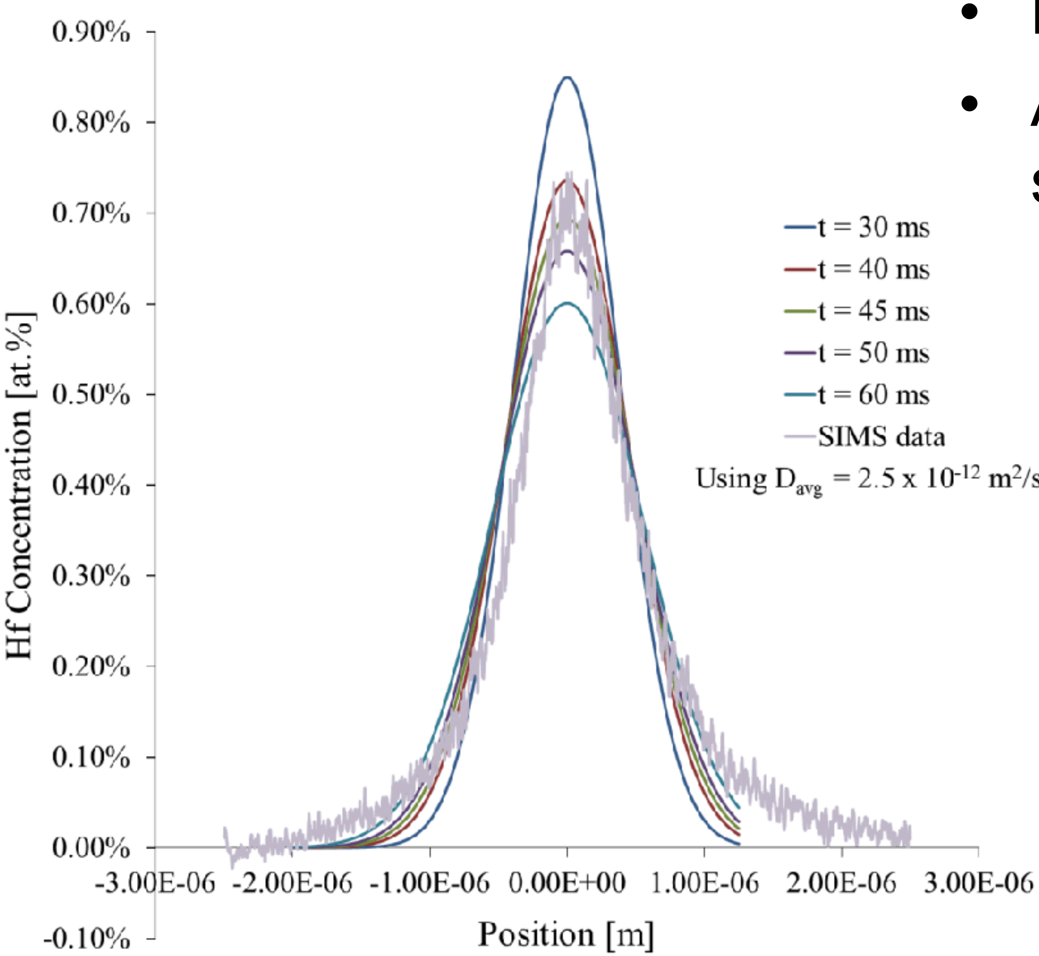
Best fit D = 2.5 x 10^{-12} m^2/s

Diffusion model



- Integrated profile across 40 nm path at location shown
- 80 kx, EDS
- Best fit D = 2.5×10^{-12} m^2/s

Diffusion model – Compare to SIMS data



- Best fit D = 2.5 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 layer species in reacted multilayers
- Resolution
  - TEM-EDS: spatial: nm, concentration: 0.1%
  - SIMS: 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