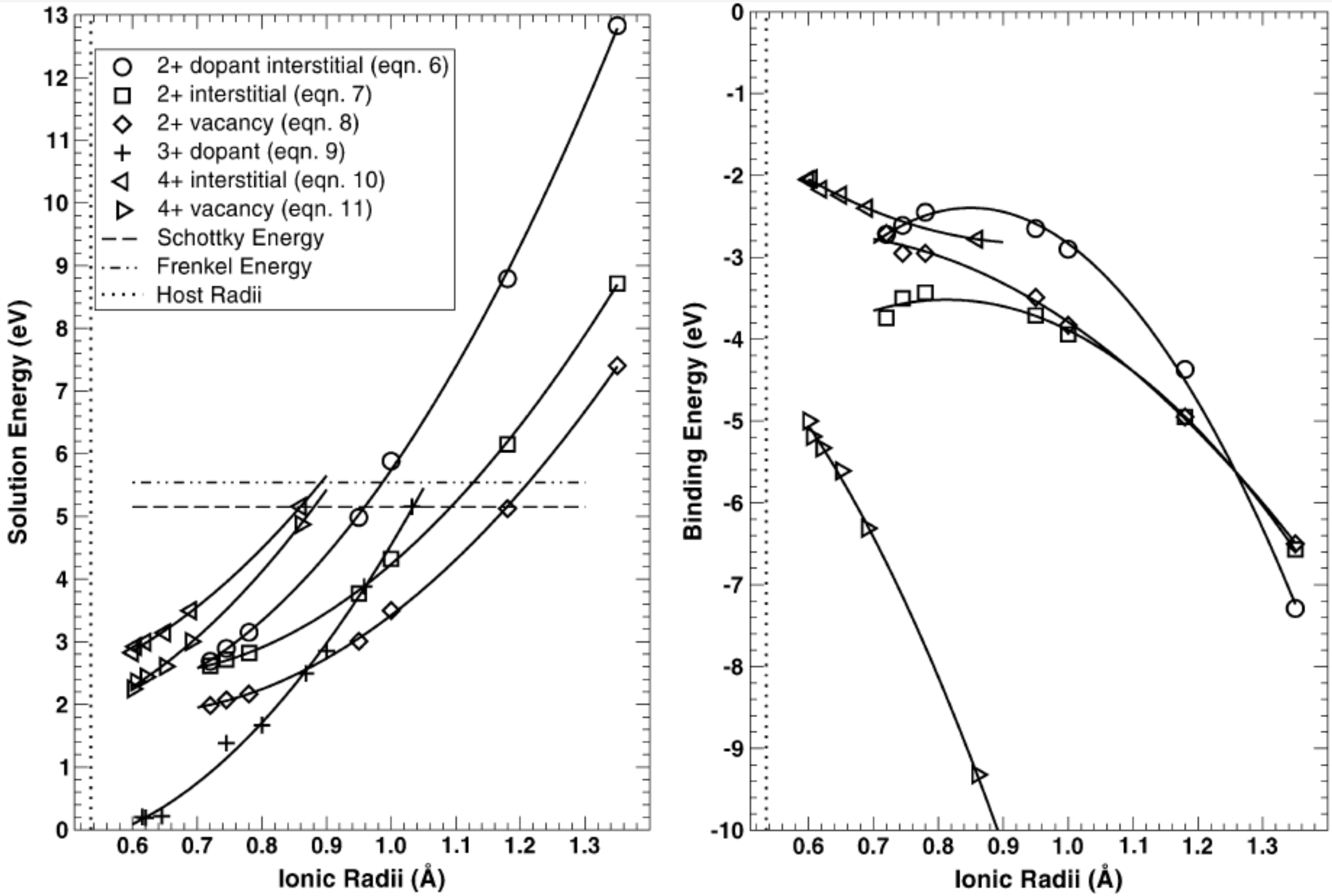
Research in Next 6-12 Months

- G.B. thermal conductance in doped samples
  - Bi crystals
  - Polycrystals
- Continue Diffusion in Al_2O_3 (Cr^{3+}, $O^{2-,\ 18}$)
  - Approximate ΔS
- Diffusion in Ni-W
  - Borisov Model $\Delta H_{GB} \sim \Delta H_L - \gamma$ (w/o complexions)
  - Complement Lehigh/Clemson-UCSD work

Defects in Alumina

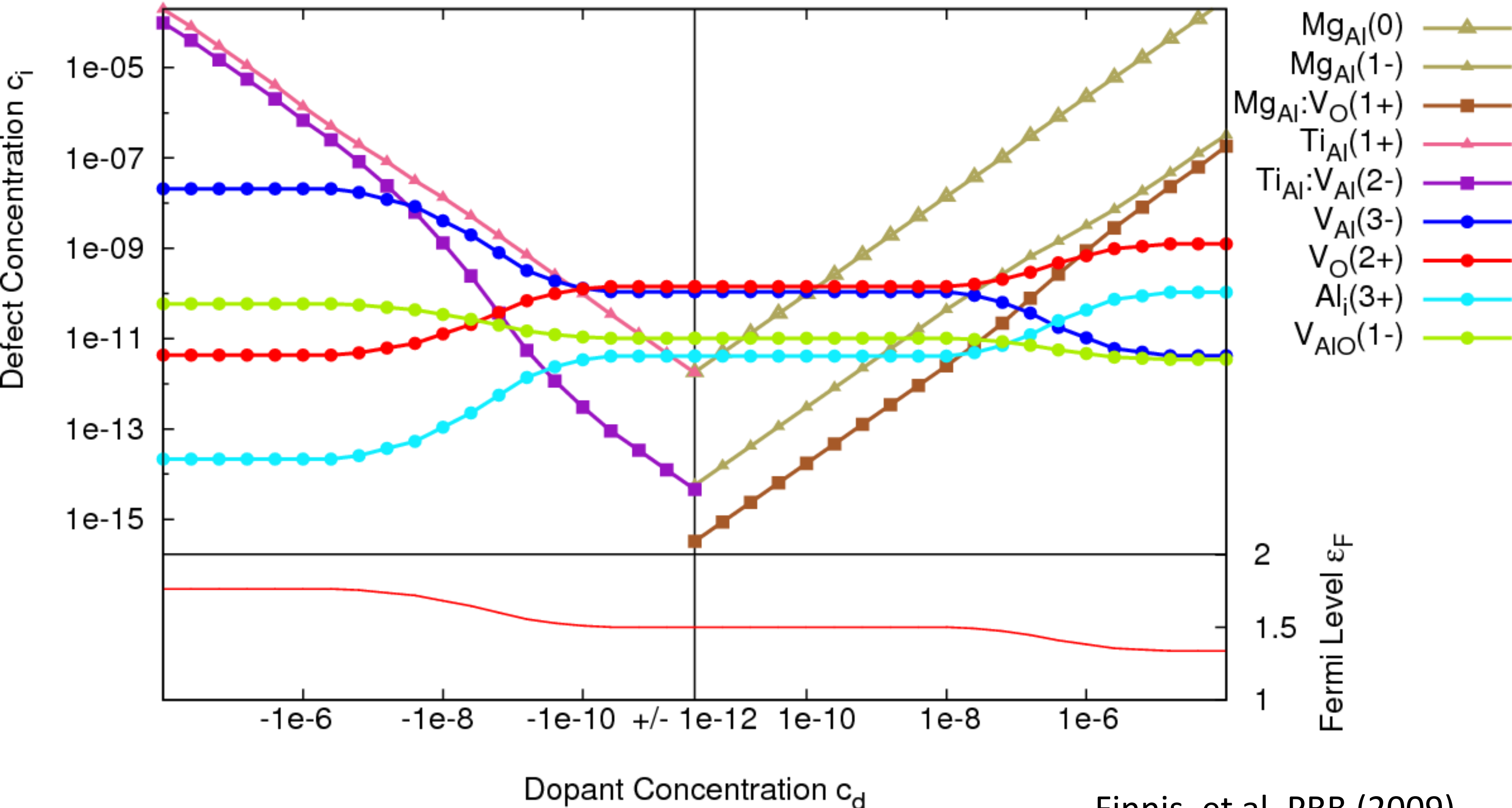


(a) Isolated Solution Energies

(b) Cluster Binding Energies

Atkinson, *JECerS* 2003

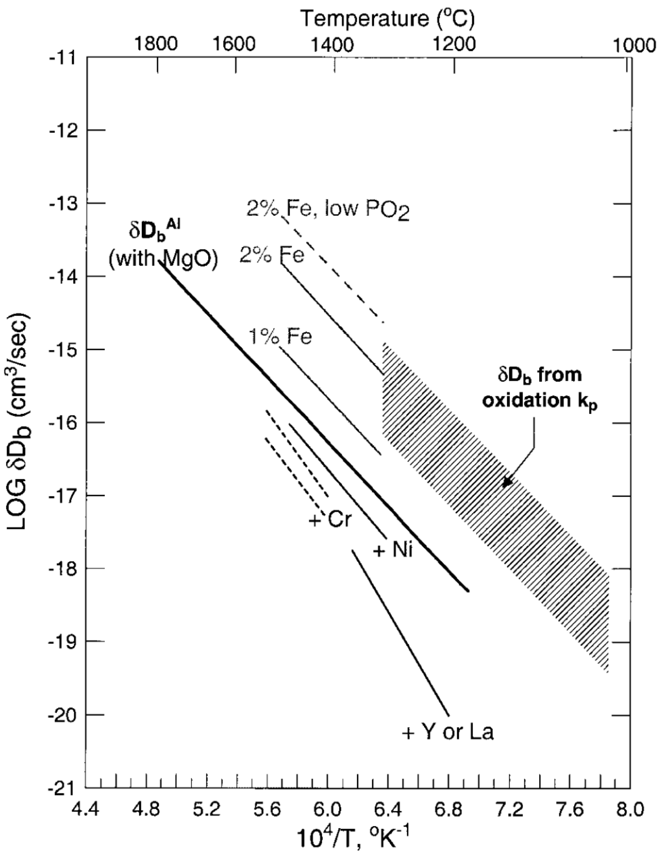
Defects in Alumina



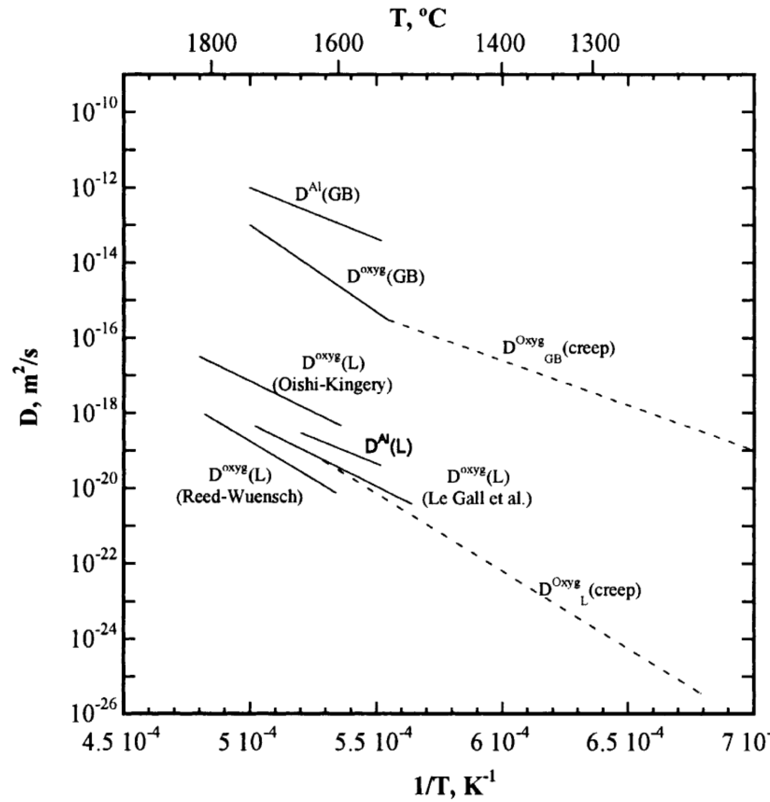
Finnis, et al. PRB (2009)

Fraction of mobile defects in Si^{4+} at 1400 ~10^{-11}

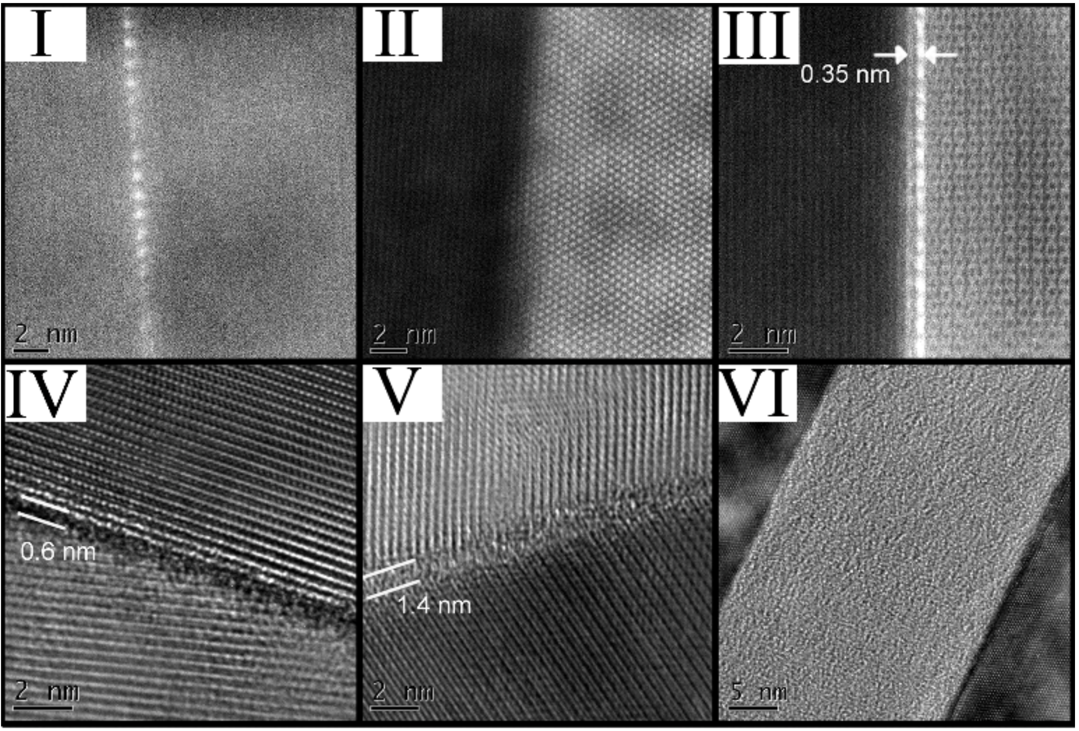
P. Hou



O. Ruano, J. Wadsworth, and O. Sherby



Alumina Diffusion - Motivation



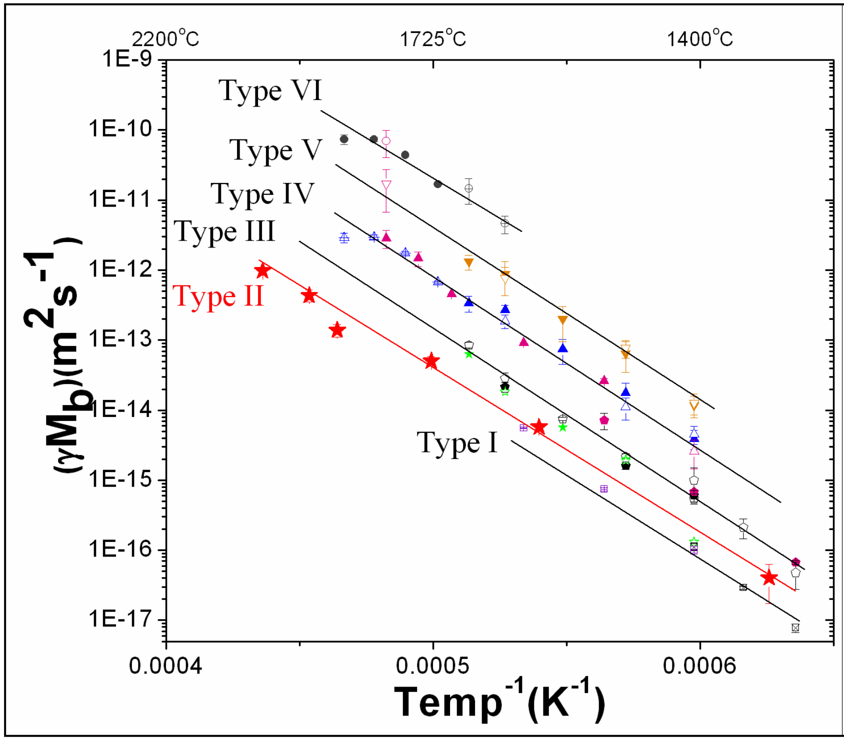
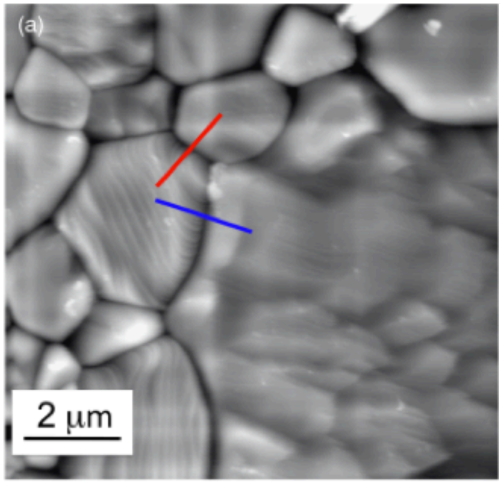
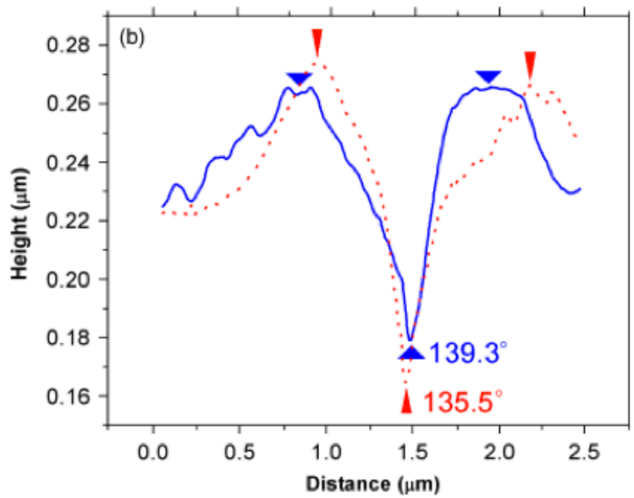


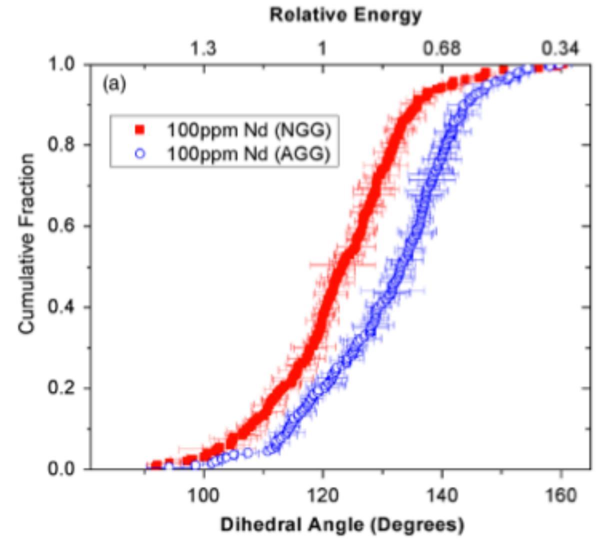
Table I. The Mean Relative Energies of Different Grain-Boundary Complexions Occurring as Normal and Abnormal Grains in Doped and Undoped Alumina Annealed at Different Temperatures

Chemistry	Temperature (°C)	Complexion	Relative energy	% energy change (complexion transition)
Undoped	1400	II (NGG)	1.11	
	2020	II (NGG)	1.08	
100 ppm-Nd_2O_3	1400	I (NGG)	0.95	−16
	1400	III (AGG)	0.8	
100 ppm-Y_2O_3	1400	I (NGG)	0.57	−46
	1400	III (AGG)	0.31	
500 ppm-MgO	1400	I (NGG)	1.07	−26
	1700	III (NGG)	0.79	
30 ppm-CaO	1200	I (NGG)	0.82	−20
	1200	III (AGG)	0.69	
200 ppm-SiO_2	1200	I (NGG)	0.68	−10
	1200	III (AGG)	0.61	

Relative Grain Boundary Energies







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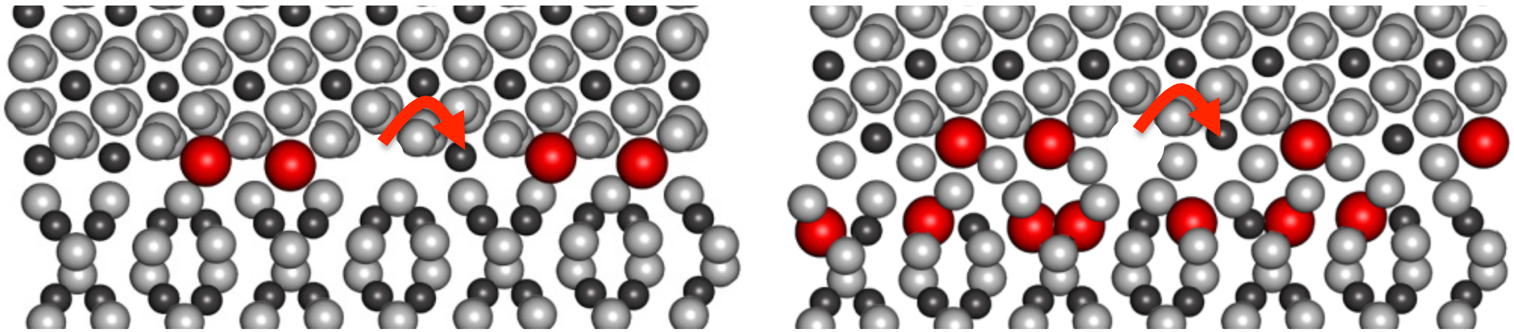
	1200	III (AGG)	0.61	
30 ppm-CaO	1400	III (NGG)	1.02	0.1
	1400	IV+ (AGG)	1.02	
	1400	III (Basal plane)	0.77	
200 ppm-SiO_2	1400	III (NGG)	0.65	9.5
	1400	IV (AGG)	0.71	
200 ppm-SiO_2	1750	IV (NGG)	0.98	−1.7
	1750	V+ (AGG)	0.96	

Dillon et al. *JACerS* (2012)

Rohrer et al. continuing more detailed analysis

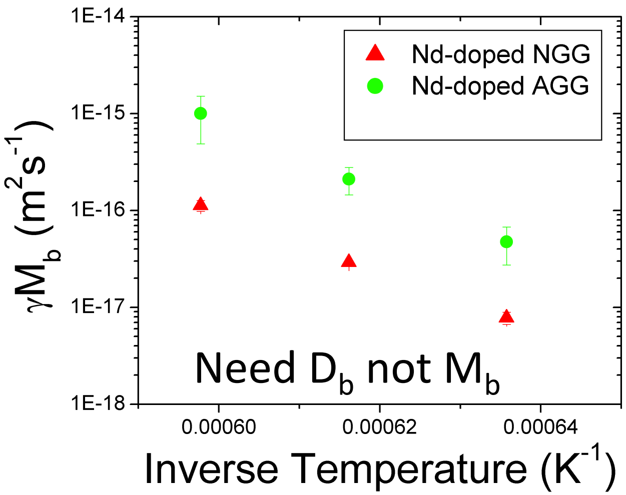
Comparing Complexions (ΔH & ΔS)

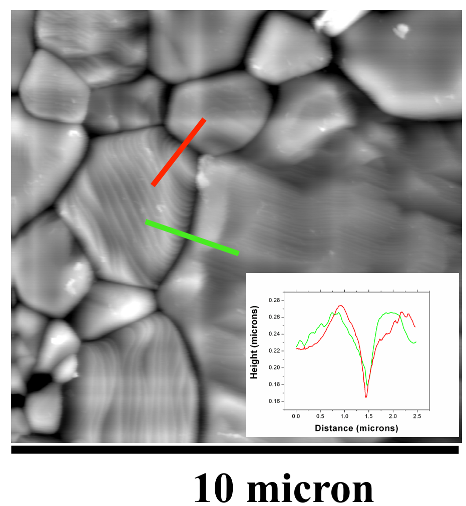


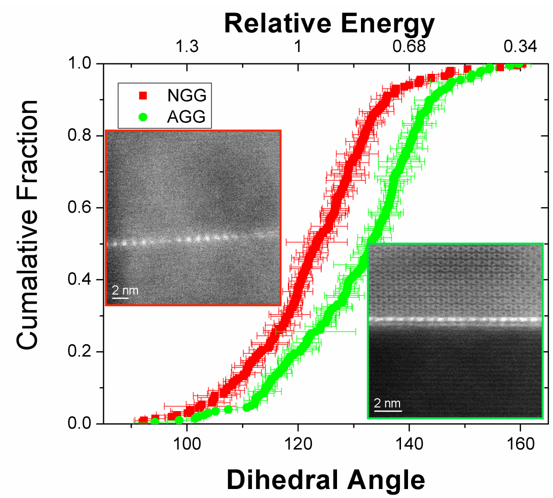
$$\Delta\gamma=\Delta\rho[RT\ln(g a_I^{2}\nu_I^{*}/g\kappa_{II}a_{II}^{2}\nu_{II}^{*})-T(\Delta S_{f,I}-\Delta S_{f,II})+(\Delta H_{f,I}-\Delta H_{f,II})+(\Delta H_{m,I}-\Delta H_{m,II})]$$

Simplifying Assumptions: $\Delta\gamma=\Delta\rho[-T(\Delta S_{I}-\Delta S_{II})+(\Delta H_{I}-\Delta H_{II})]$

Approach:

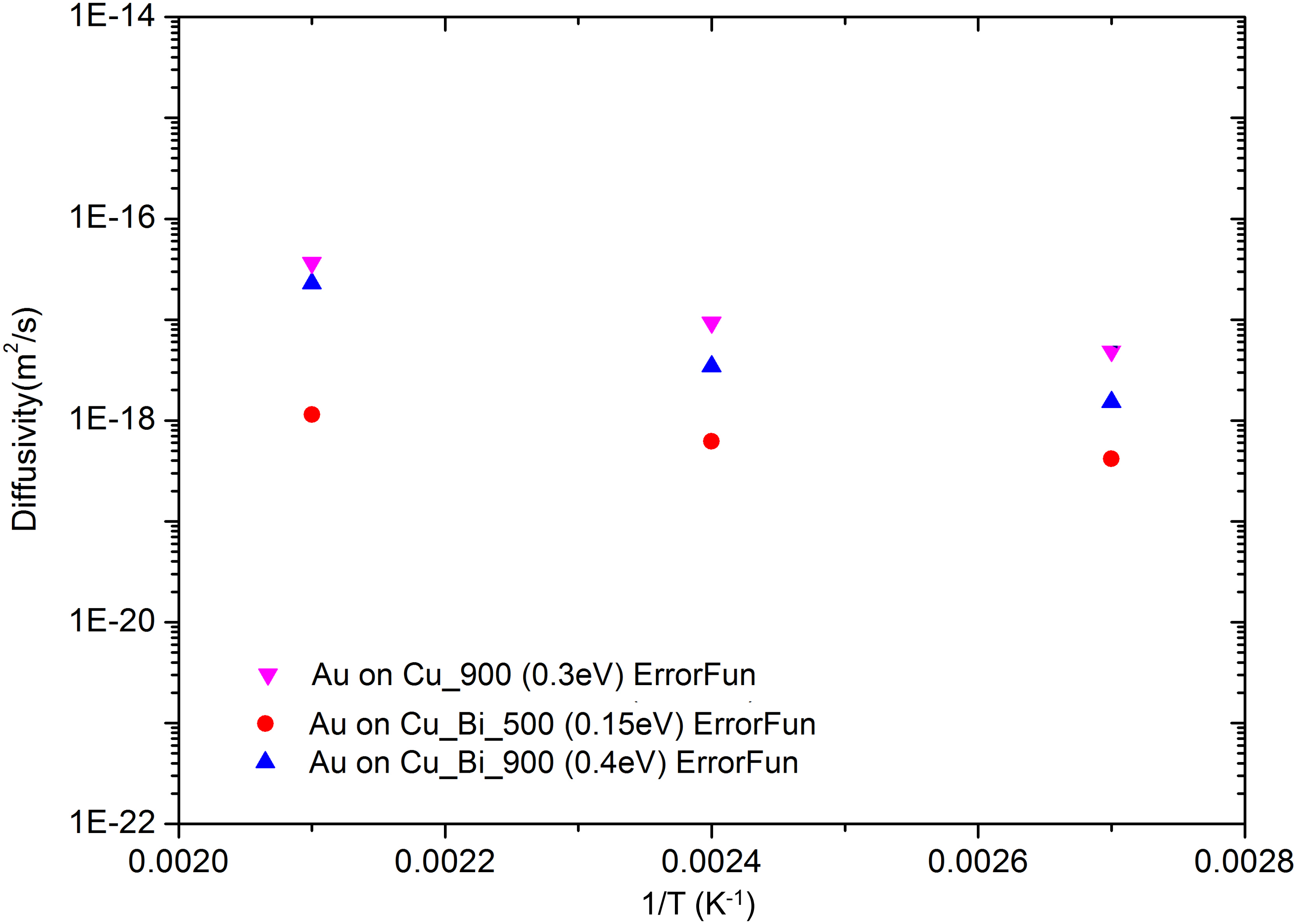






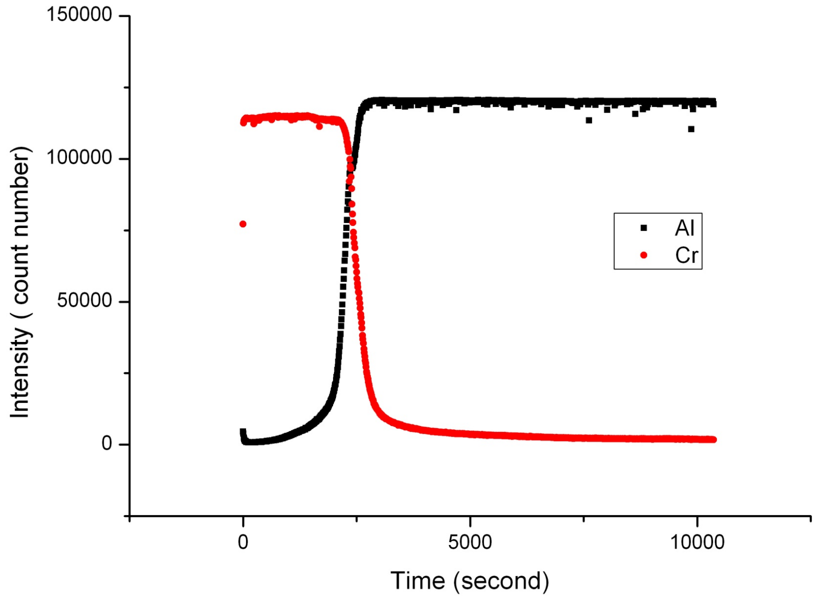
Check: $\gamma=\rho[RT\ln(g a_b^{2}\nu_b^{*}/g\kappa_I a_I^{2}\nu_I^{*})-T(\Delta S_I-\Delta S_b)+(\Delta H_I-\Delta H_b)+(P\Delta V_I-P\Delta V_b)]$

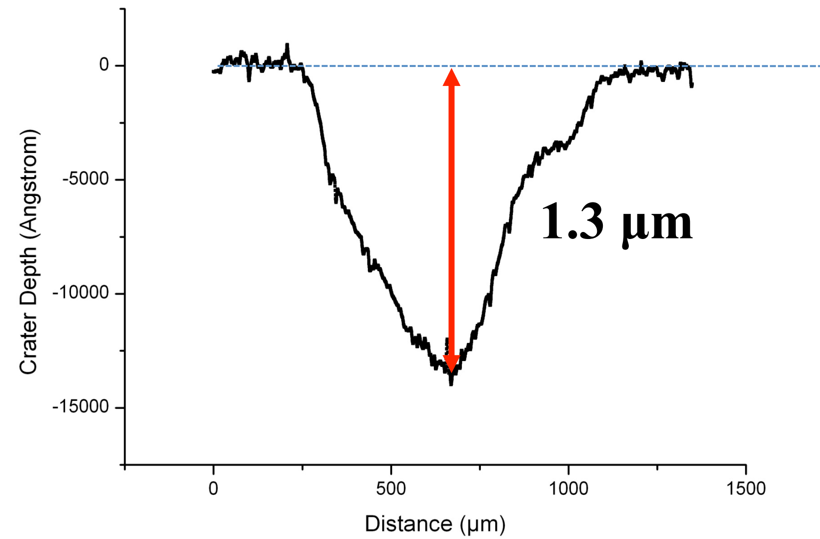
Diffusion in Bi doped Cu

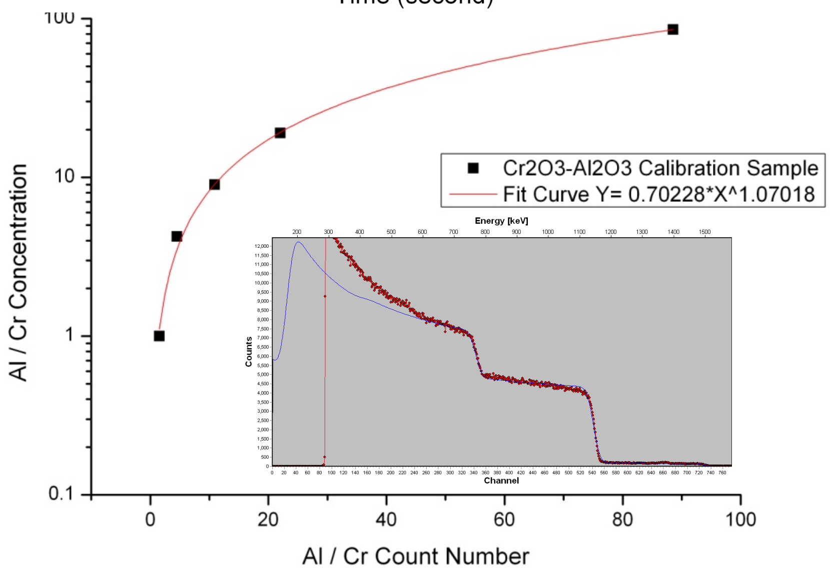


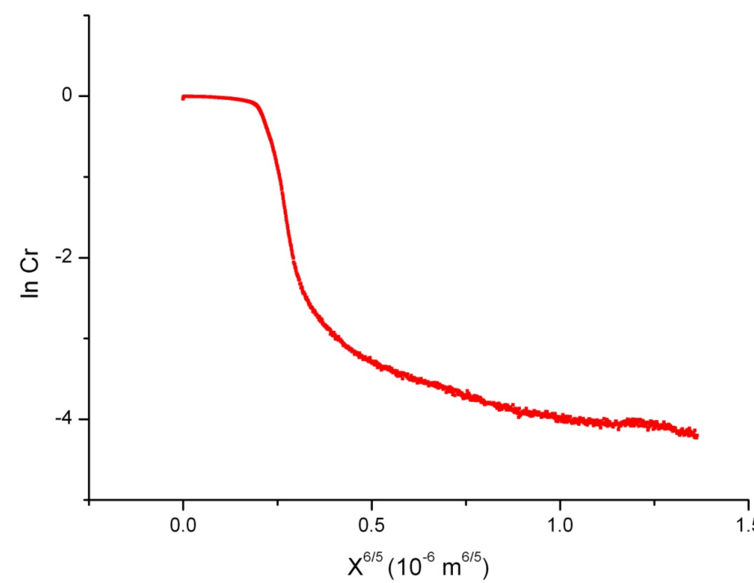
Au diffusivity-temperature dependence in the Cu(Bi) alloys

Cr^{3+} Diffusion in Al_2O_3

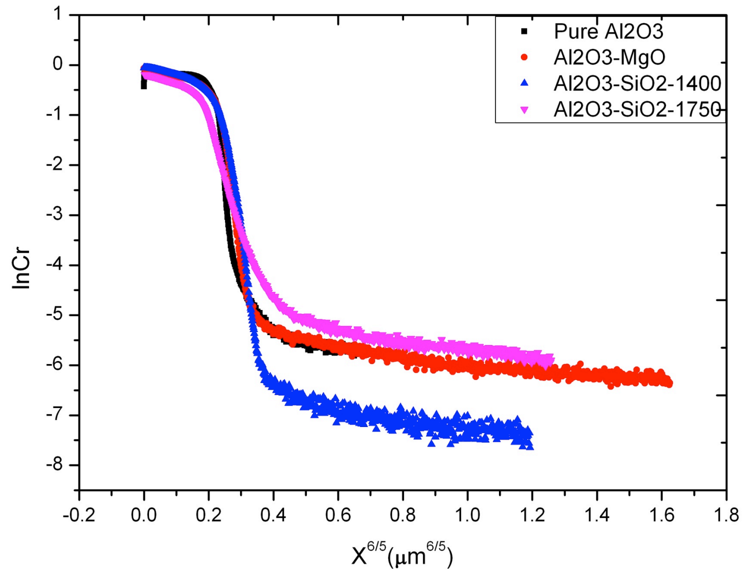


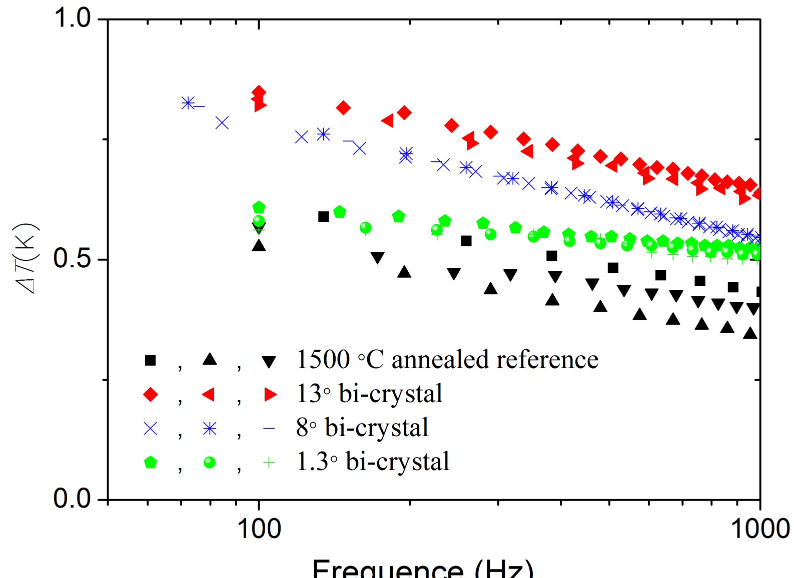


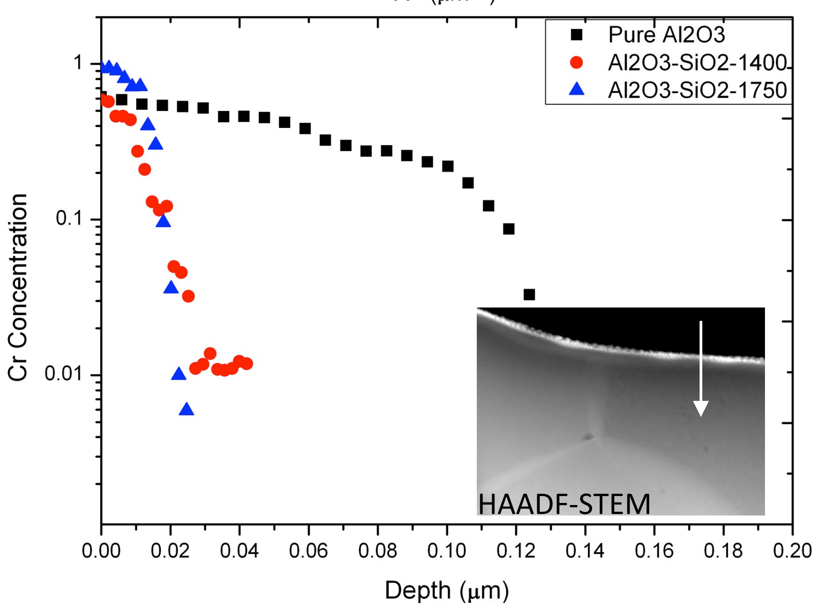


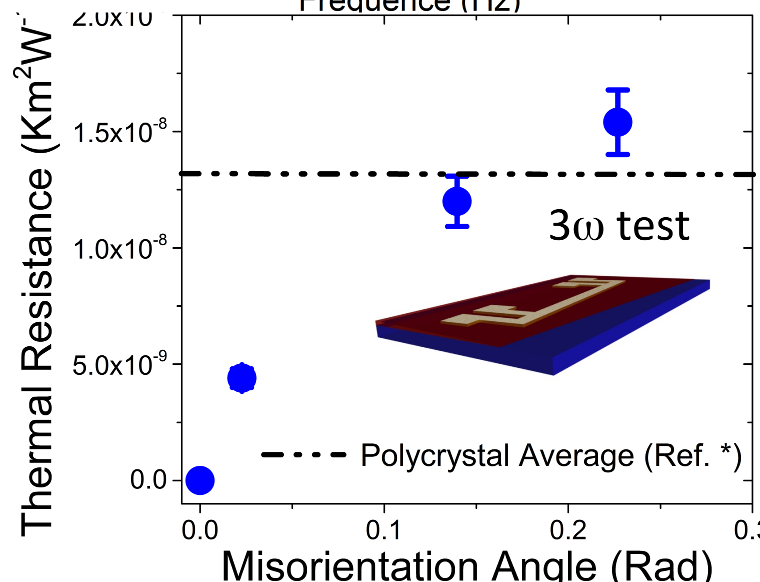


Continued Work: Obtaining D, γ, T_c in Al_2O_3 (then V*)



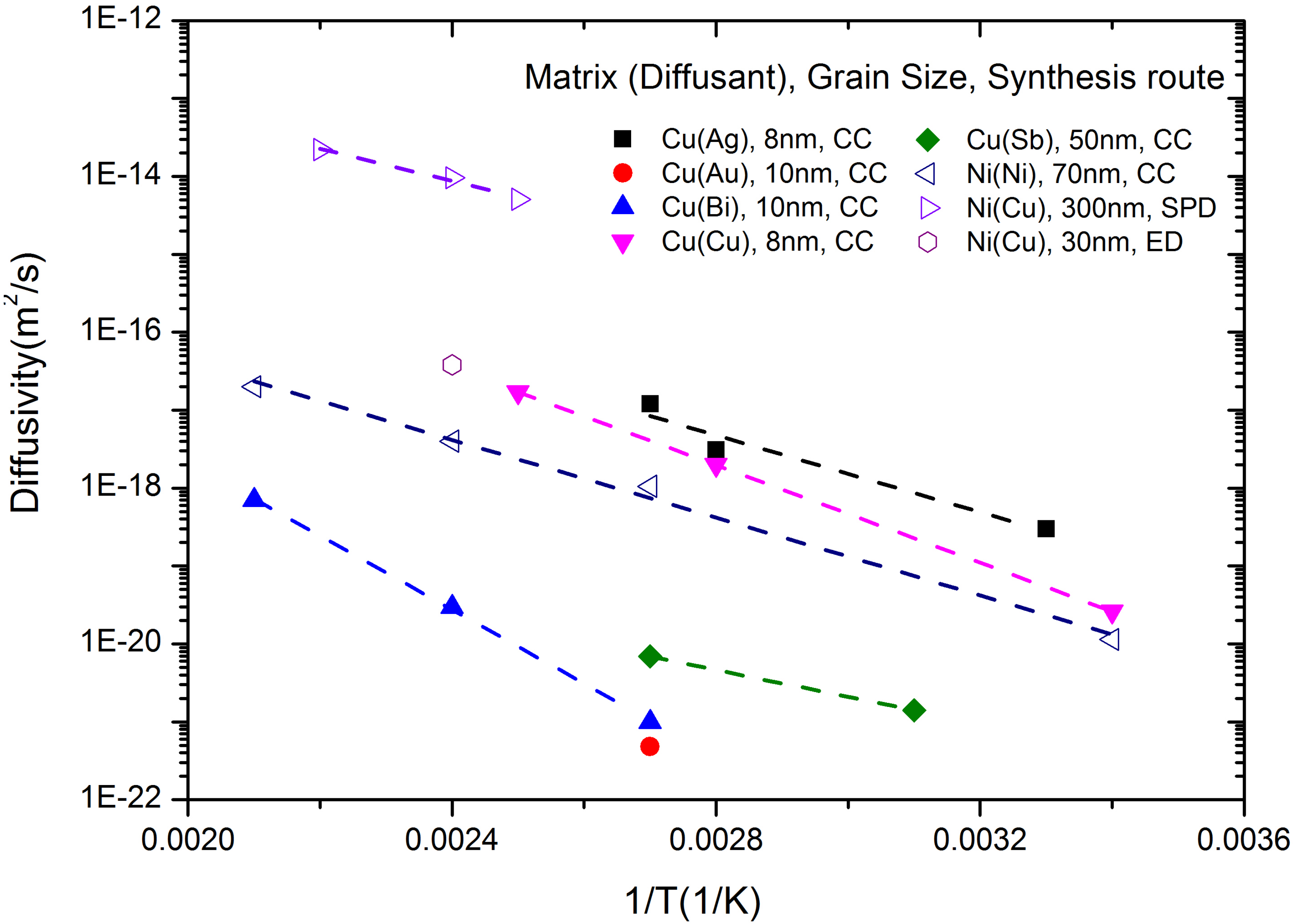






*Smith et al. *JACerS* (2003)

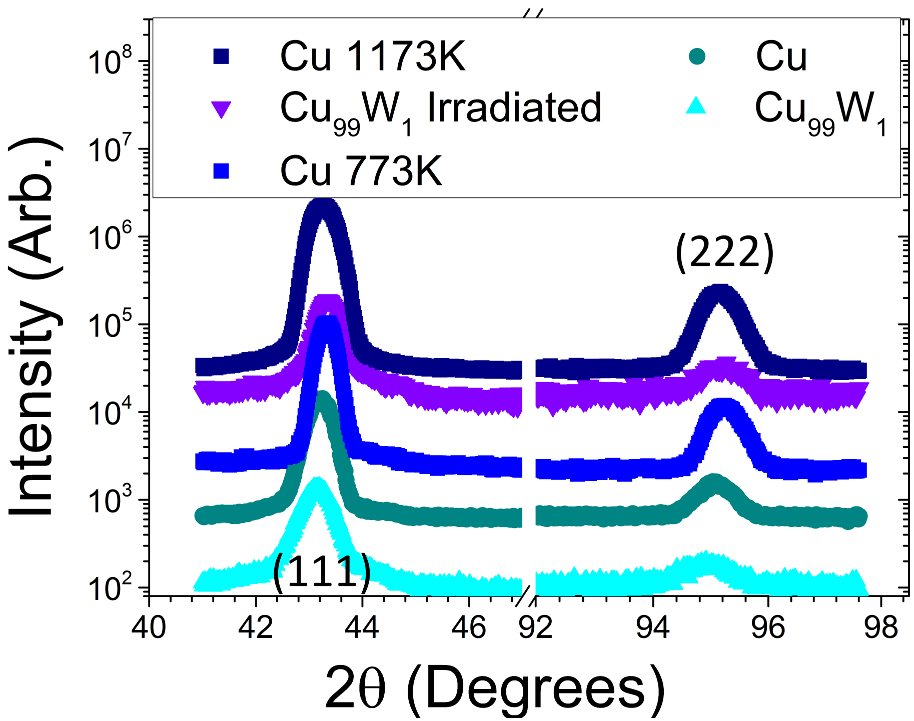
GB Diffusion Nanograin Alloys- Motivation

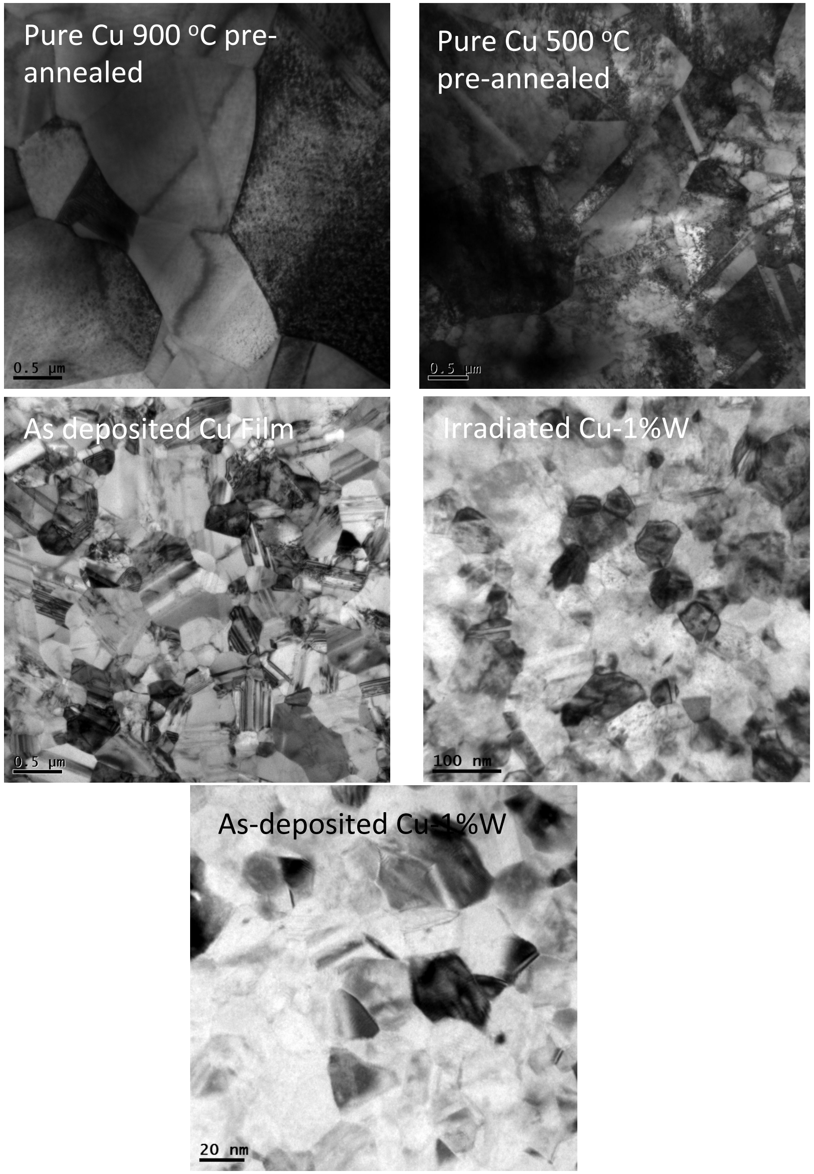


Kolobov et al. Russian J. Phys. (2008)

Wurschum, Herth, Brossmann, Advanced Engineering Materials (2003)

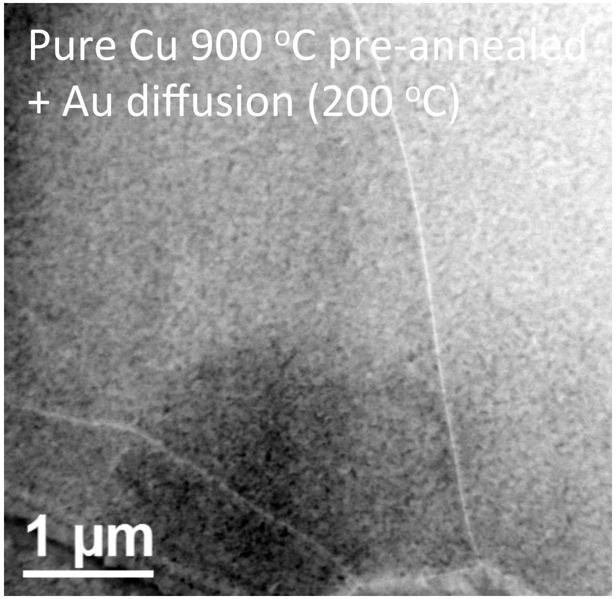
Cu of Varying Grain Size

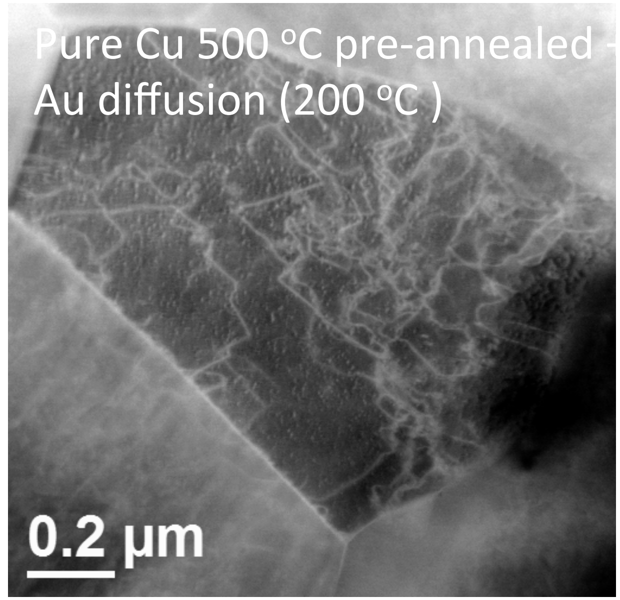


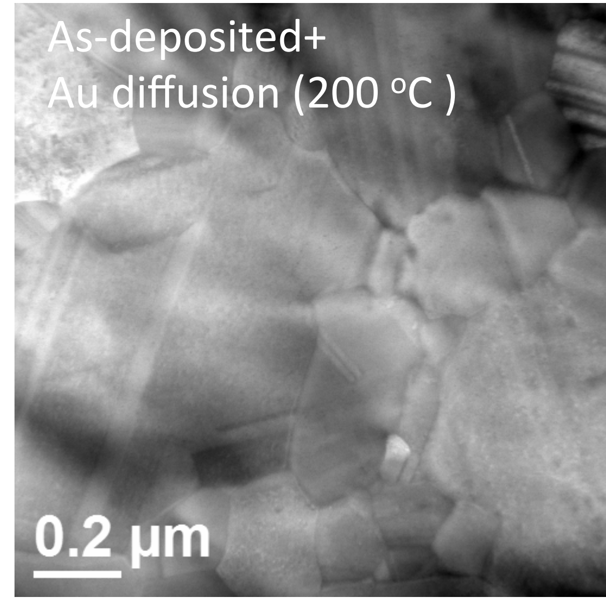


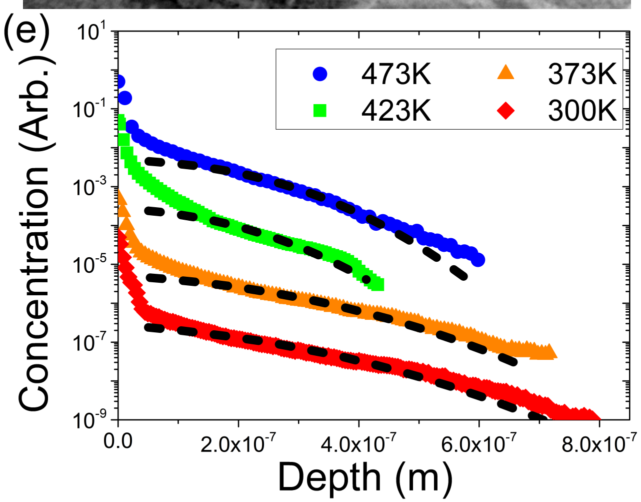
Sample	Average Grain Size (nm)		
	X-ray	TEM	
		w/o twins	w/ twins
Cu	15.0	~150	~20
Cu-W	14.7	~30	~15
Irrad. Cu-W	17.0	~80	~25
773K Cu	23.5	~2000	~280
1173K Cu	47.0	~4000	~550

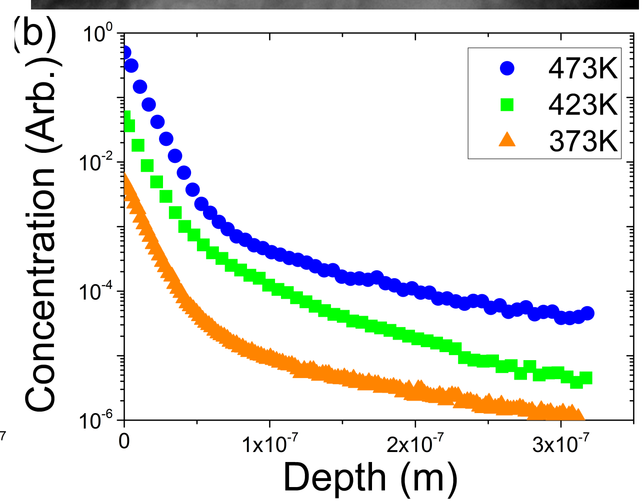
Au diffusion in Cu (Different G.S.'s)

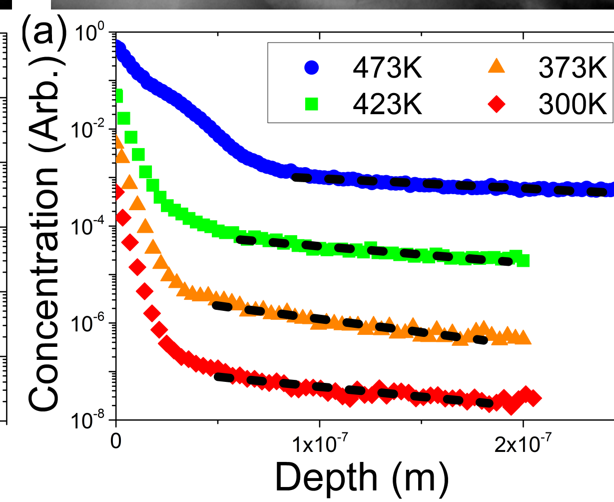










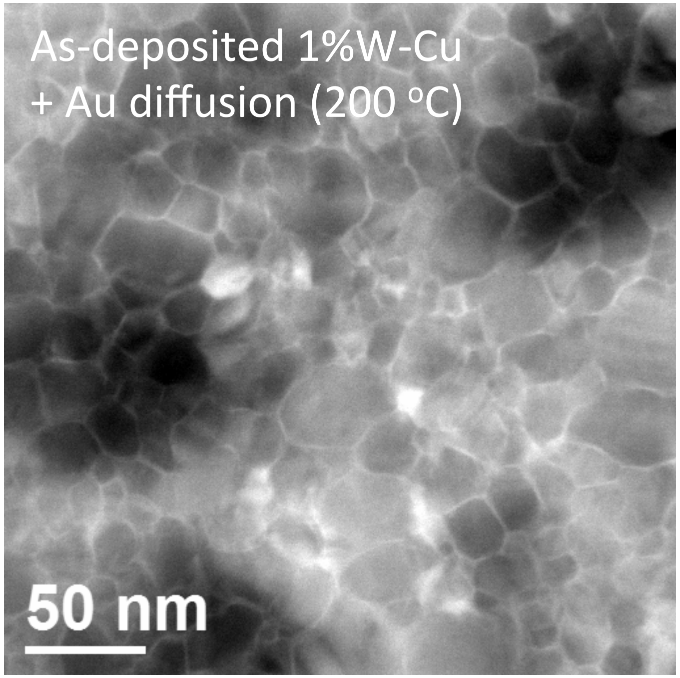


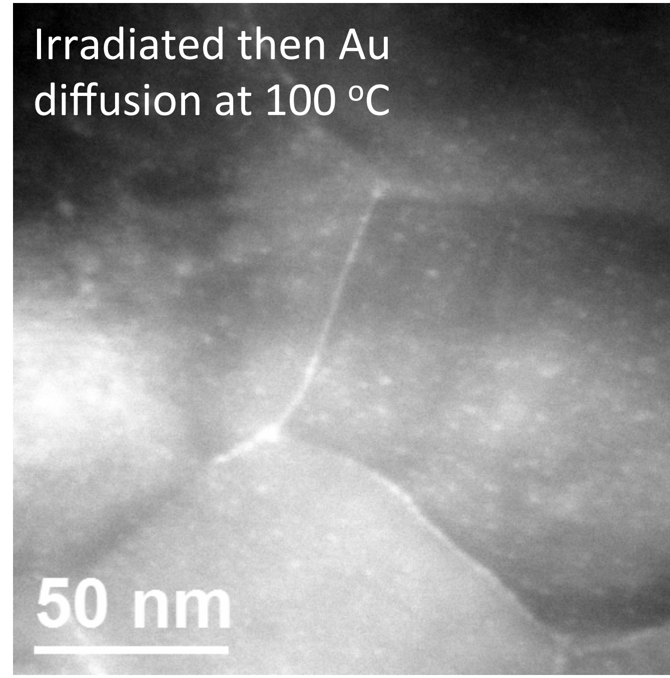
$$\bar{c}(z) \approx \bar{c}_{gb}(z) \propto \mathrm{erfc}\left(\frac{z}{2\sqrt{D_{gb}t}}\right)$$

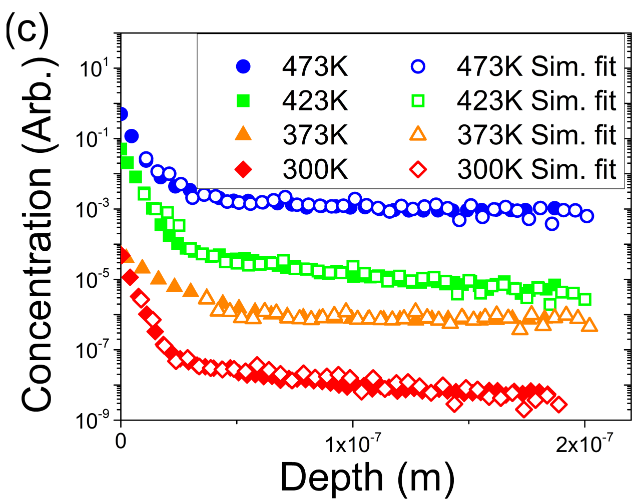
No Model

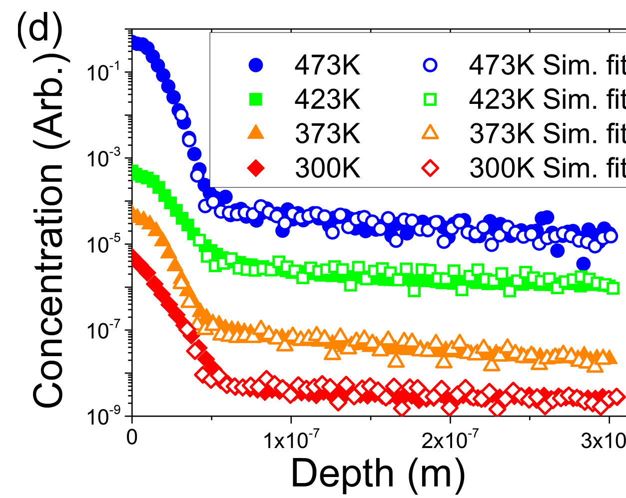
$$\delta D_b = v\left(\frac{\partial \ln \bar{c}}{\partial z}\right)^{-2}$$

Au diffusion in Cu (Different G.S.'s)

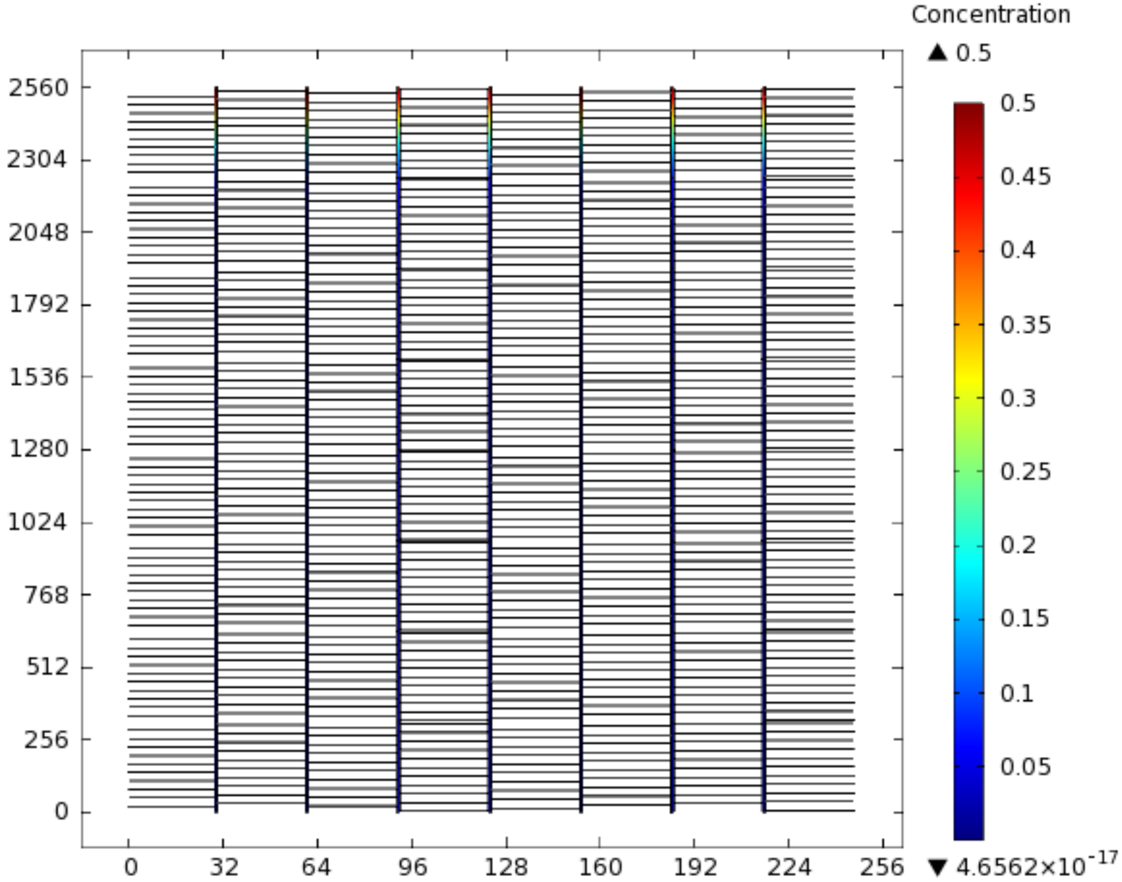


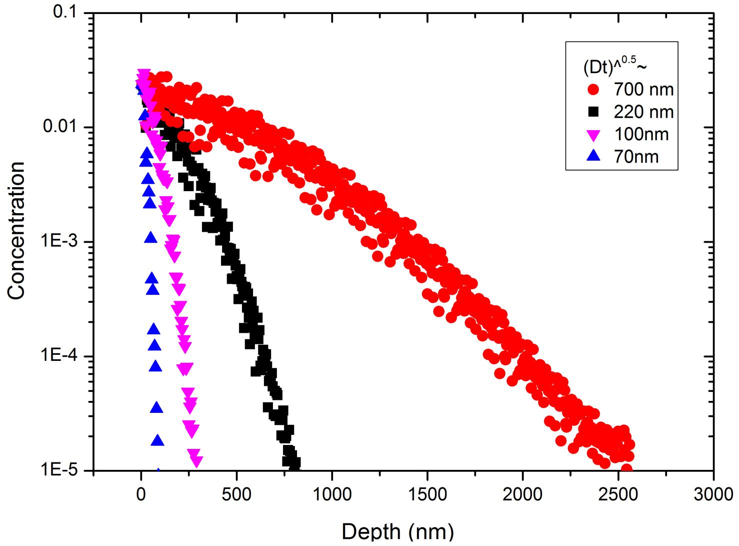


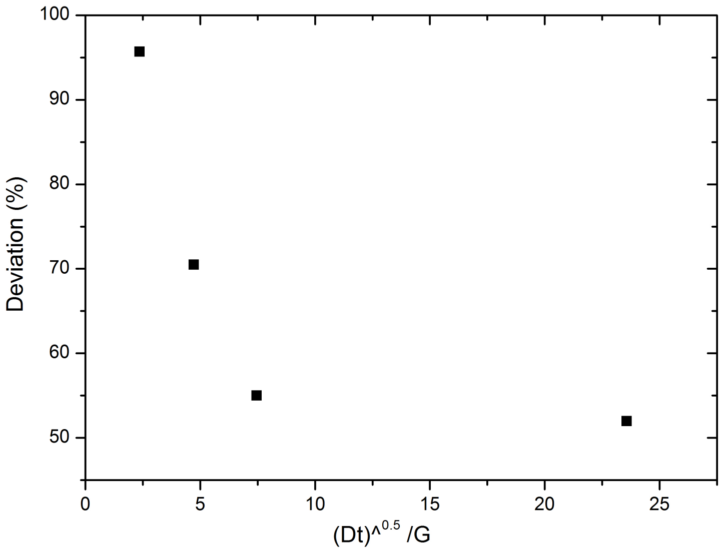




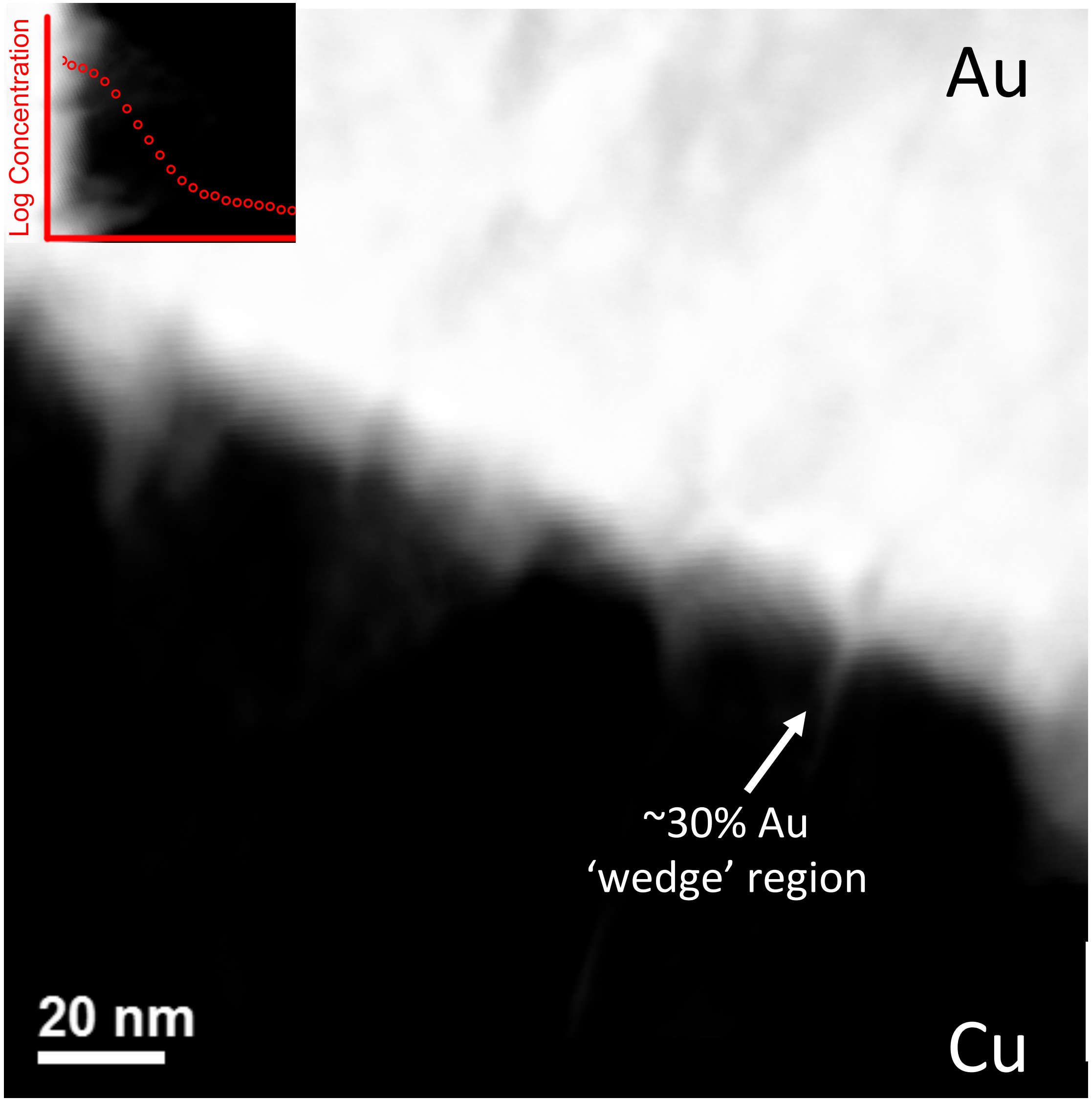
FE Simulation Nanograin Diffusion



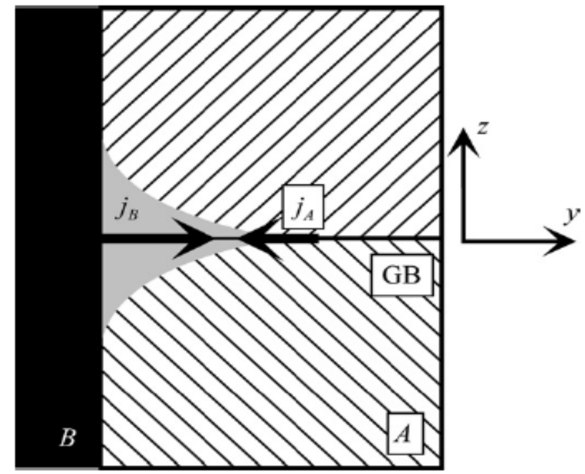




Grain Boundary Kirkendall Effect



Kirkendall Effect induced G.B. migration/lattice drift



A-B
Inequality Diffusion

$$j_A = -\frac{D_A n_A}{kT}\frac{\partial \mu_A}{\partial y}; \quad j_B = -\frac{D_B n_B}{kT}\frac{\partial \mu_B}{\partial y},$$

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial y^2} + \frac{D_B C_B \Omega}{kT}\frac{\partial^2 \sigma}{\partial y^2} + \frac{\Omega D_B}{kT}\frac{\partial C_B}{\partial y}\frac{\partial \sigma}{\partial y}$$

Klinger, *Acta Mater.* 2011

Finite Element Simulation

Grain boundary diffusion in thin film model:

Near surface (10~20nm) D_{sb} different from D_b in film