Grain Boundary Diffusion in Cu and Cu-Bi

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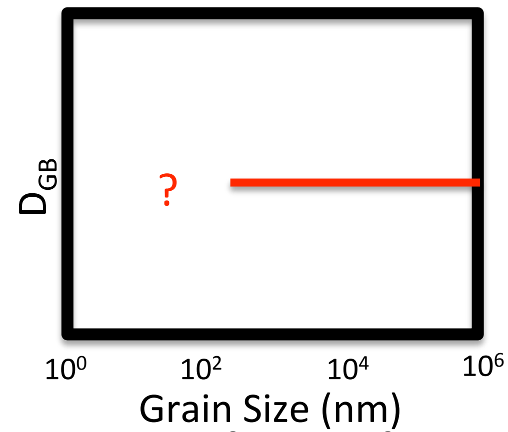
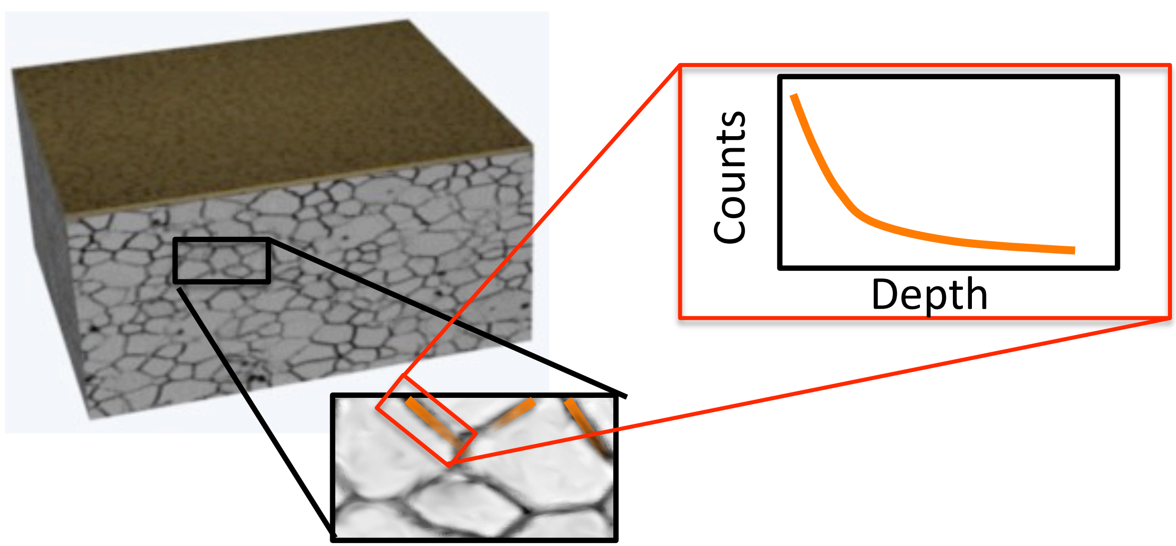
Carnegie Mellon University

Research Topics

- Quantifying 'nanoscale effect' on G.B. diffusion
  - Scaling effect?
  - 'G.B. relaxation'
  - AGG effects on D?



- Characterizing G.B. diffusion in Bi-doped Cu

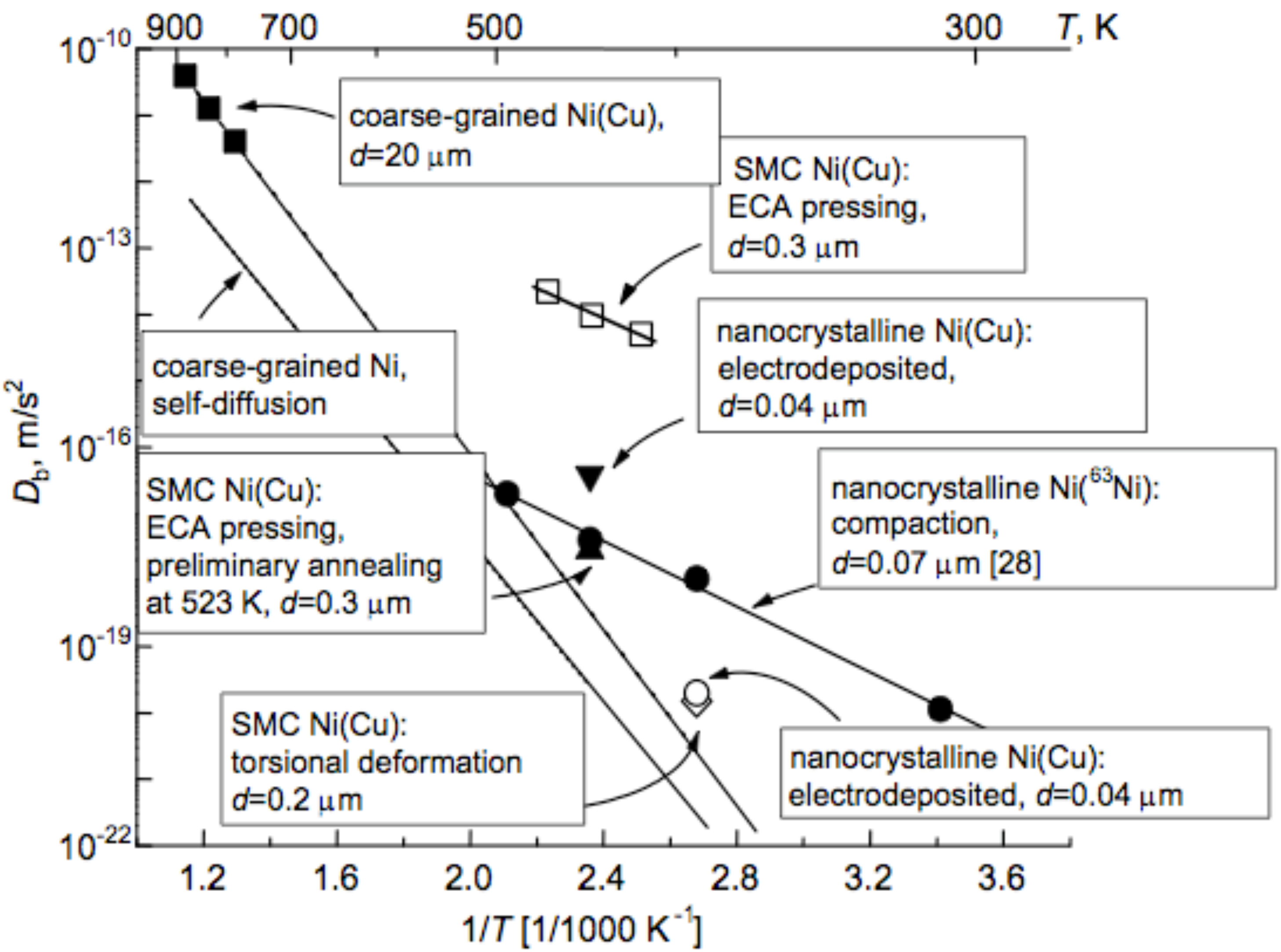


Variation in Nano G.B. Diffusion Results (Cu)

Part A: Metals	Synthesis	T_a [K]	T_d [K]	D (0.25 T_M) [m^2s^{-1}]	Model	d [nm]	Method
Pd (Fe)[17] [a]	CC	373 [f]	423–523	2.8×10^{-20}	C	50 [c]	RT
Pd (Fe) [18] [a]	SPD	293–673	371–623	3×10^{-20}	C	80 [c]	RT
Fe (Fe) [19][a]	CC	403 [f]	452–499	1×10^{-21} [b]	C	31 [c]	RT
Fe (Fe) [19][a]	SPD	527	527	3×10^{-19} (0.29T_M) [b]	C	NS	RT
Literature data:							
Cu (Cu) [15]	CC	AT	293–393	9.2×10^{-19}	C	8 [d]	RT
Cu (Ag) [32]	MS	NS	393–428	NS	C	20 [d]	AES
Cu [33]	CC	AT	293–420	NS		11	NMR
Cu (Ag) [16]	CC	AT	303–373	1.6×10^{-18}	C	8	EBMA
Cu (Au) [34]	CC	AT	373	4.8×10^{-22} (0.27T_M)	C	10	AES
Cu (Bi) [34]	CC	AT	293–413	3×10^{-20} [b]	C	10	RBS
Cu (Sb) [35]	CC	AT	323–373	2.4×10^{-21} [e] 1.3×10^{-22} [e]	2 IF	50	RBS
Ni (Ni) [12]	CC	773 [f]	293–473	5.9×10^{-18} [e] 1.6×10^{-19} (0.27T_M) [e]	2 IF	70	RT
Ni (Cu) [26]	SPD	398	398–448	9.6×10^{-15} (0.245T_M) [b]	C	300 [d]	SIMS
Ni (Cu) [26]	ED	NS	423	3.8×10^{-17} (0.245T_M)	C	30	SIMS
Fe (B) [36]	CC	AT	293–383	(4.5×10^{-18})	C	7	SIMS
Grain boundaries (GBs) in coarse-grained metals and bicrystals:							
fcc, general [37]				(1.7×10^{-21}) [g]			

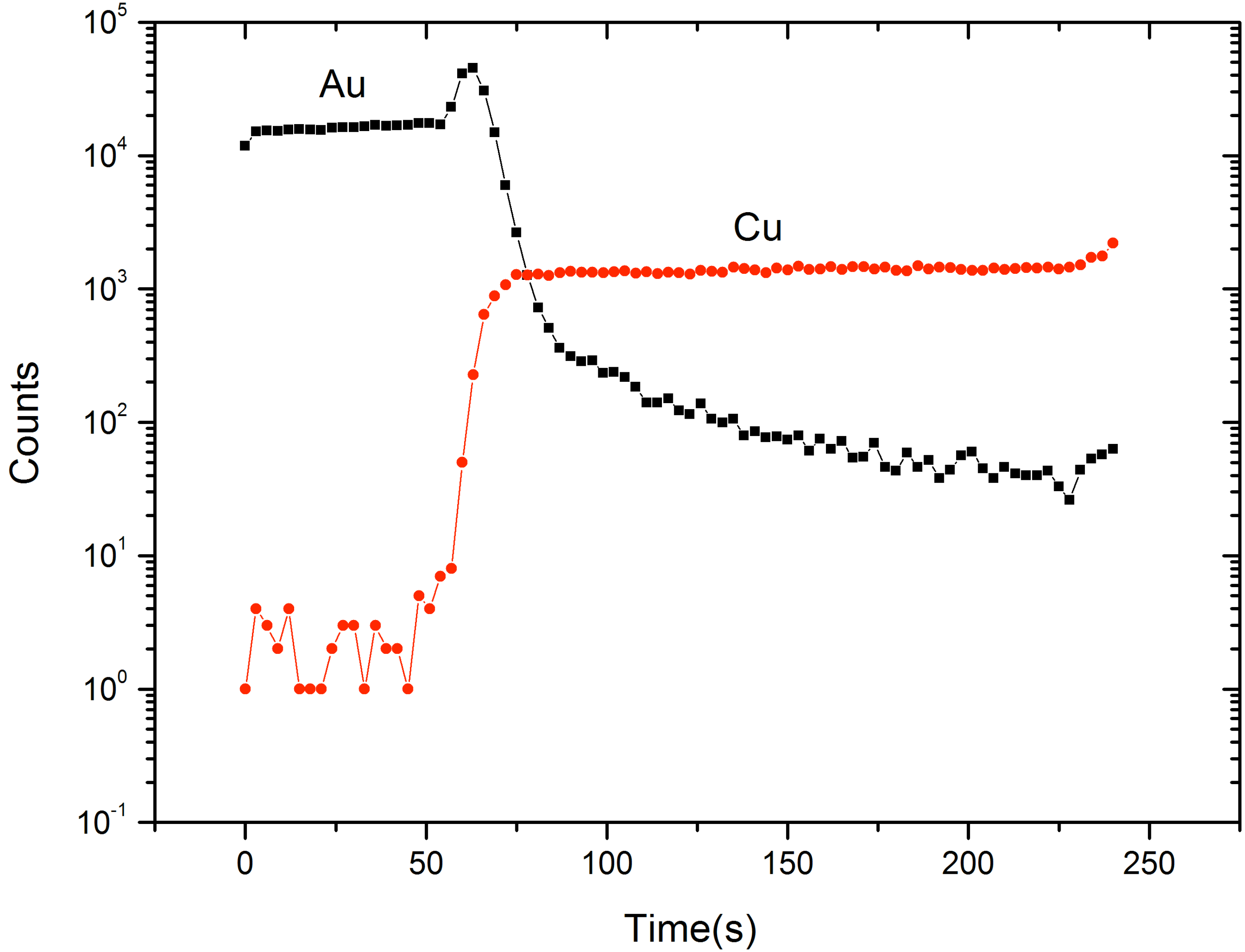
Wurschum, Herth, Brossmann, Advanced Engineering Materials (2003)

Variation in Nano G.B. Diffusion Results (Ni)

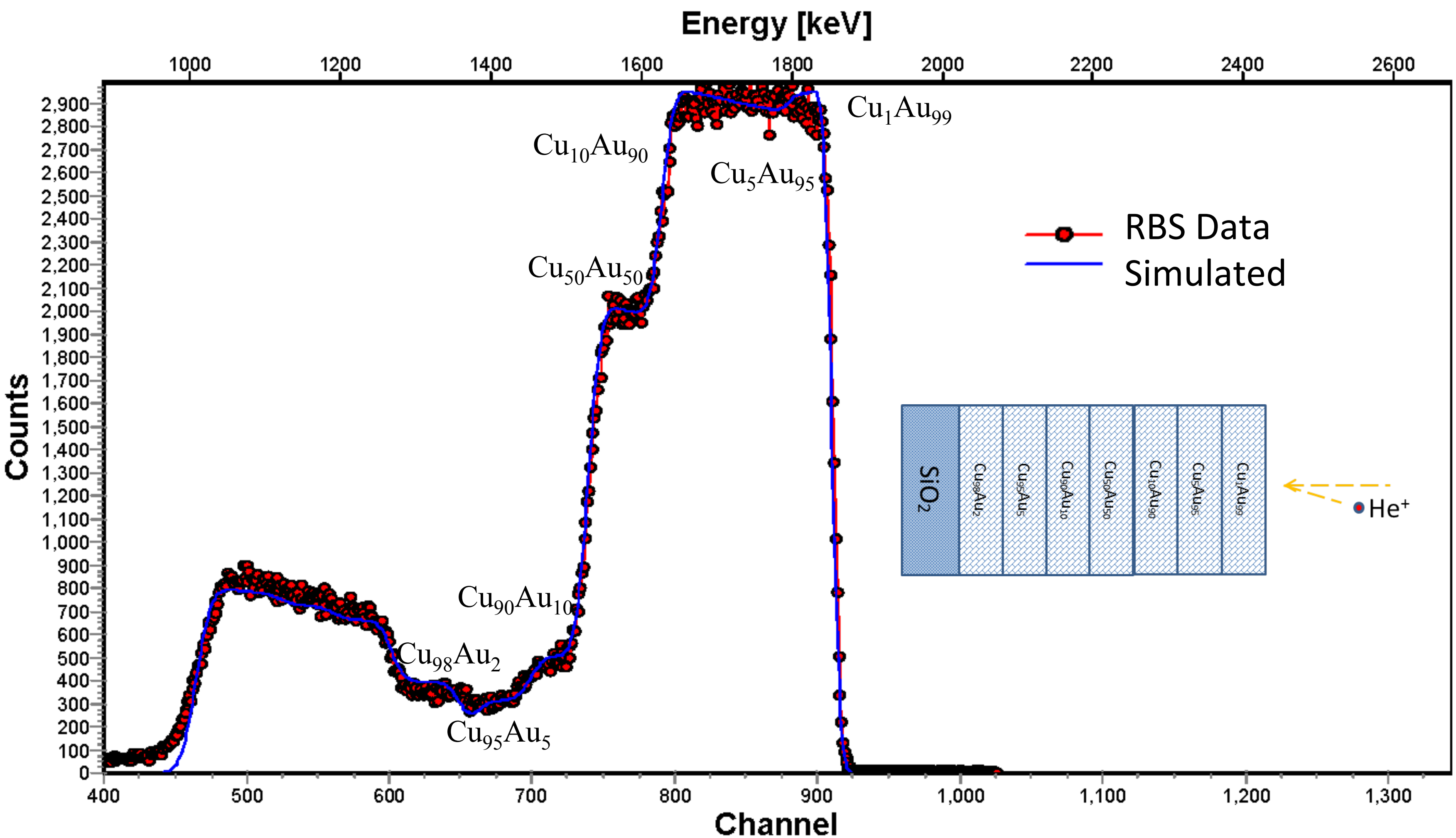


Kolobov et al. Russian J. Phys. (2008)

SIMS Raw Data

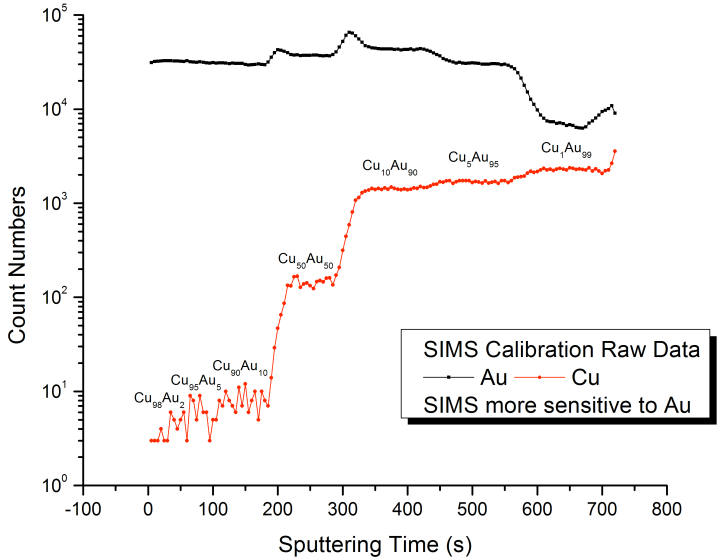


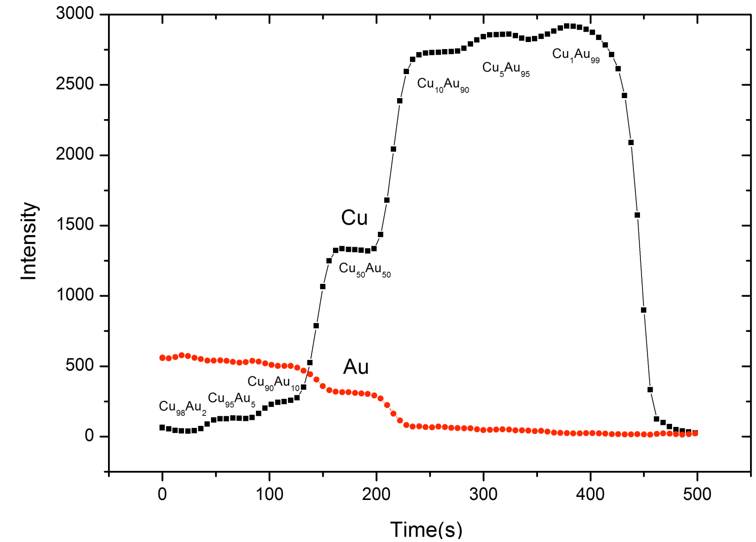
SIMS Calibration

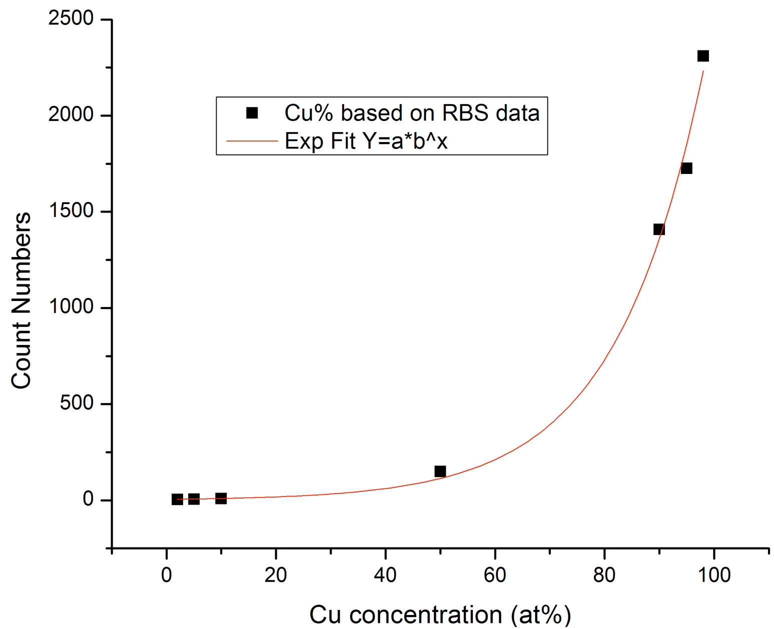


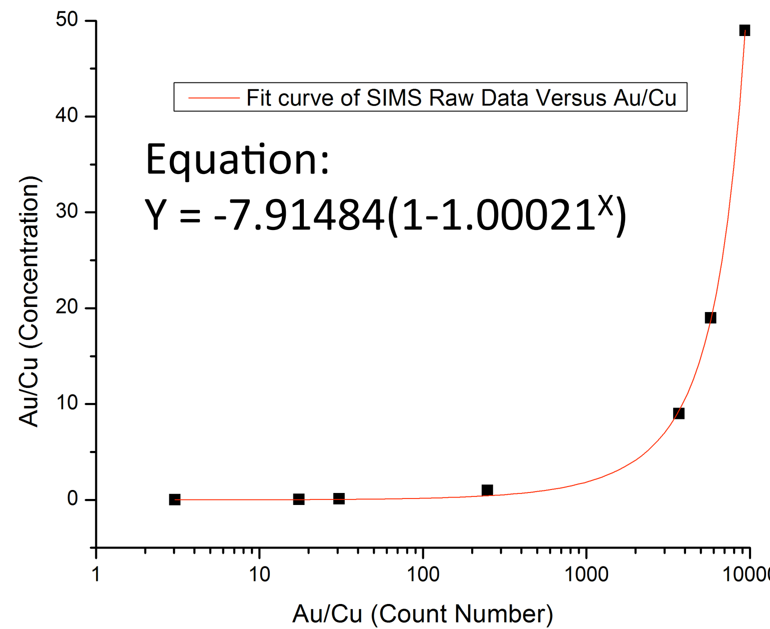
7 Multilayers Determined by RBS to Calibrate SIMS “Matrix Effect”

Calibrating SIMS from RBS



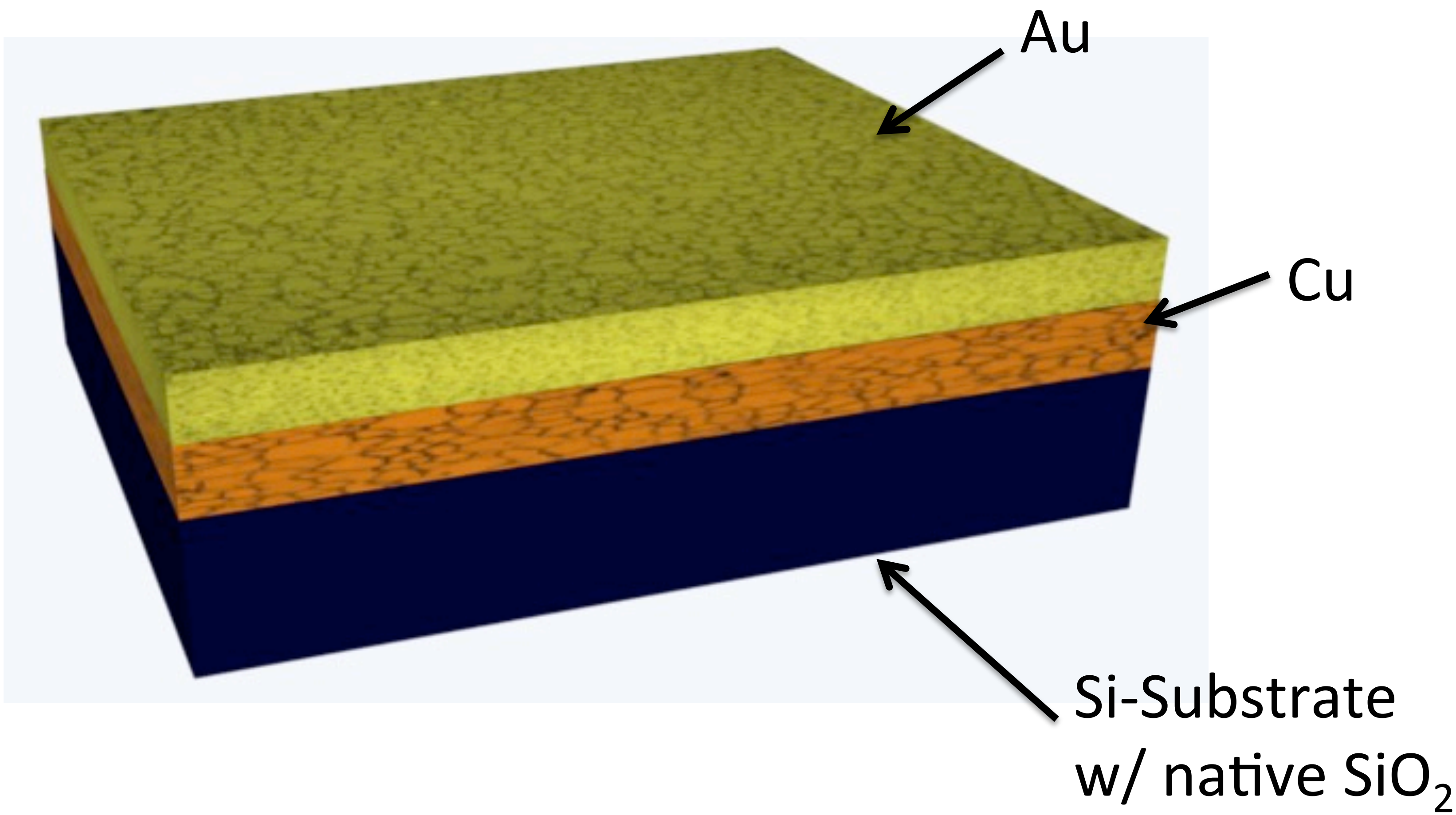






Current Experiments

Constant Source Au Diffusion into Cu



Equations for Fitting Diffusion Data

Type B

Instantaneous Source

$$sD_{gb}\delta = 1.322\sqrt{\frac{D}{t}}\left(-\partial\bar{c}/\partial z^{6/5}\right)^{-5/3}$$

Constant Source

$$sD_{gb}\delta = 1.308\sqrt{\frac{D}{t}}\left(-\partial\bar{c}/\partial z^{6/5}\right)^{-5/3}$$

Type C

Instantaneous Source

$$\bar{c}(z) \approx \bar{c}_{gb}(z) \propto \exp\left(-\frac{z^2}{4D_{gb}t}\right)$$

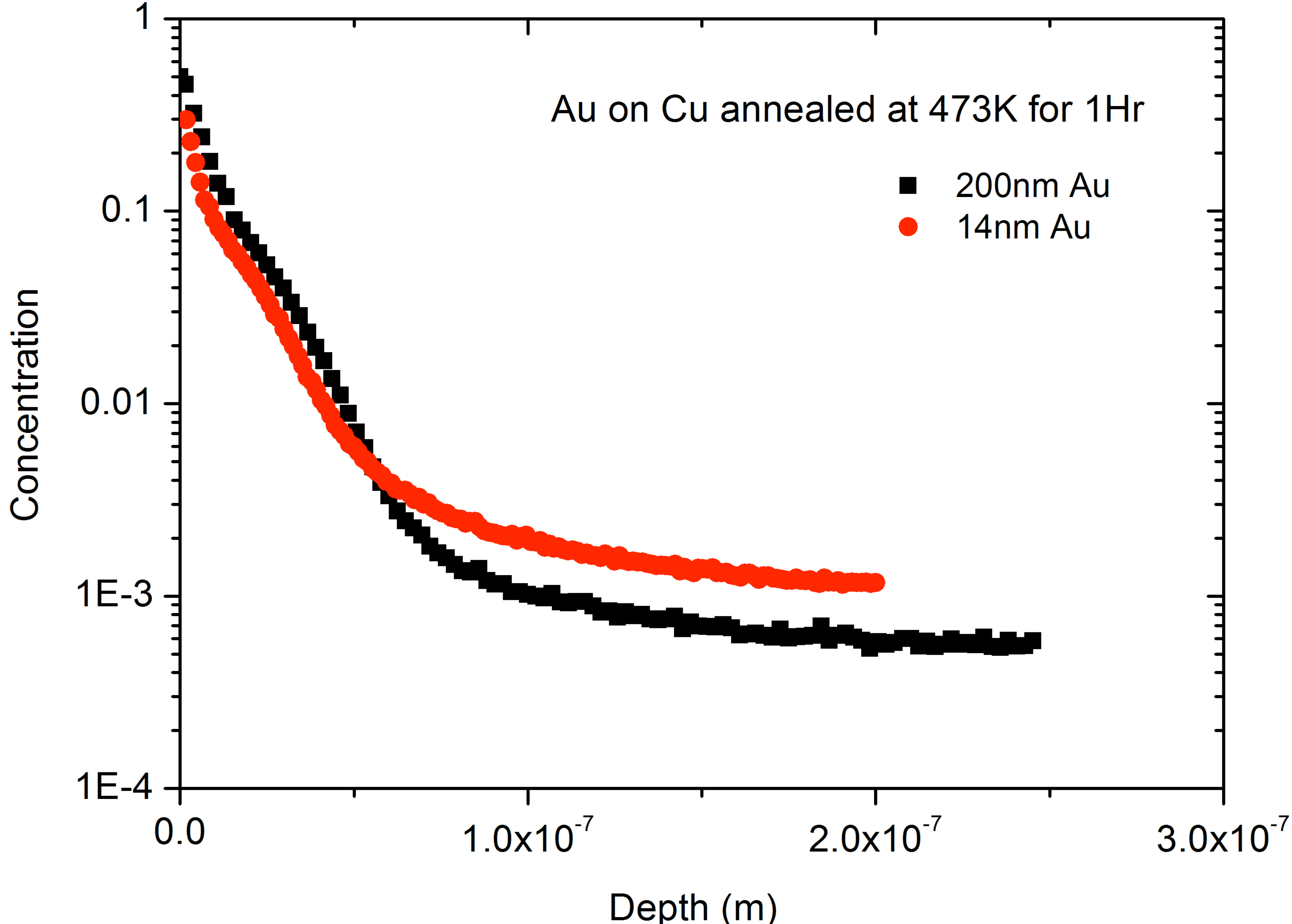
Constant Source

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

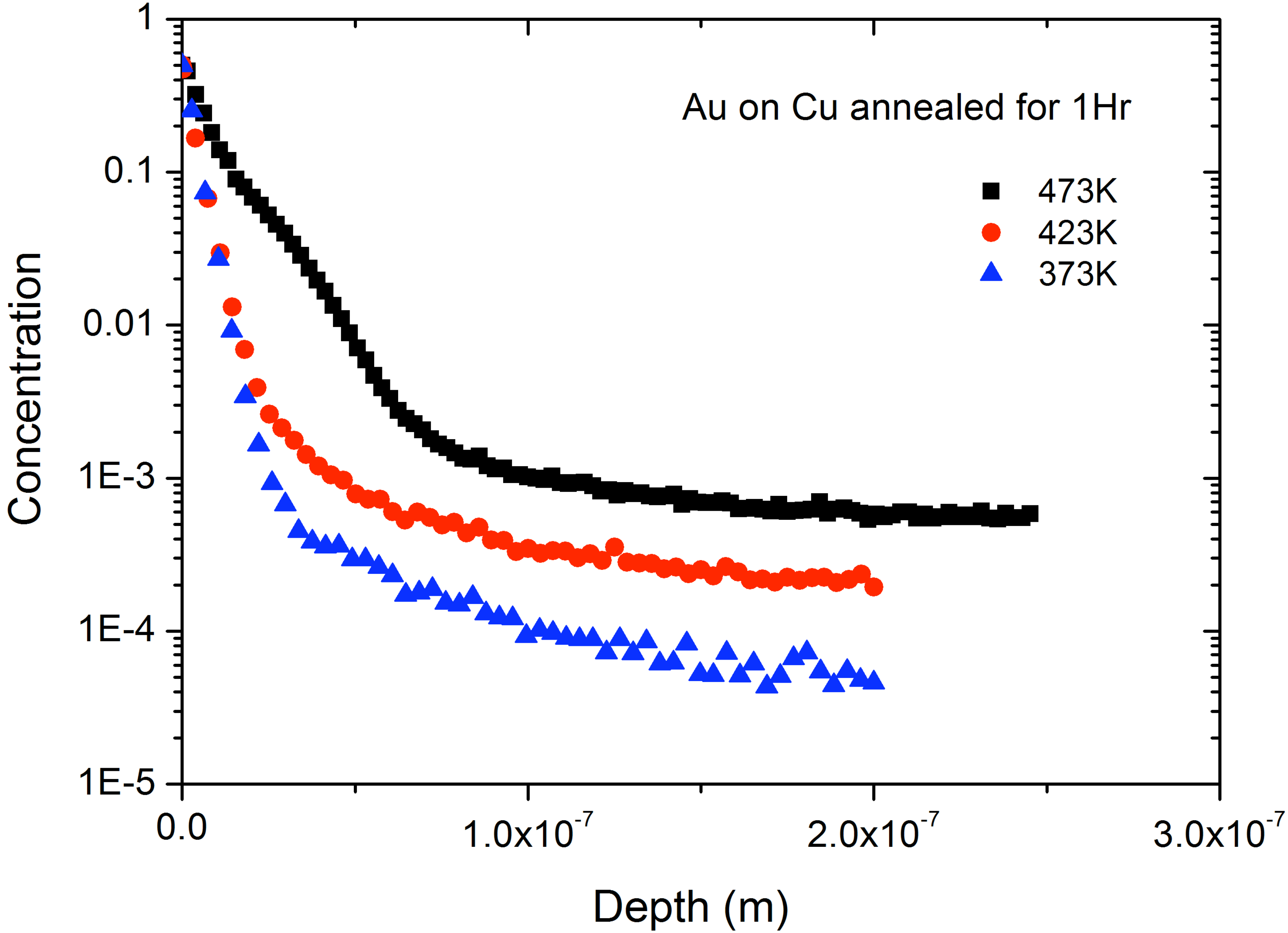
Mobile Grain Boundaries

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

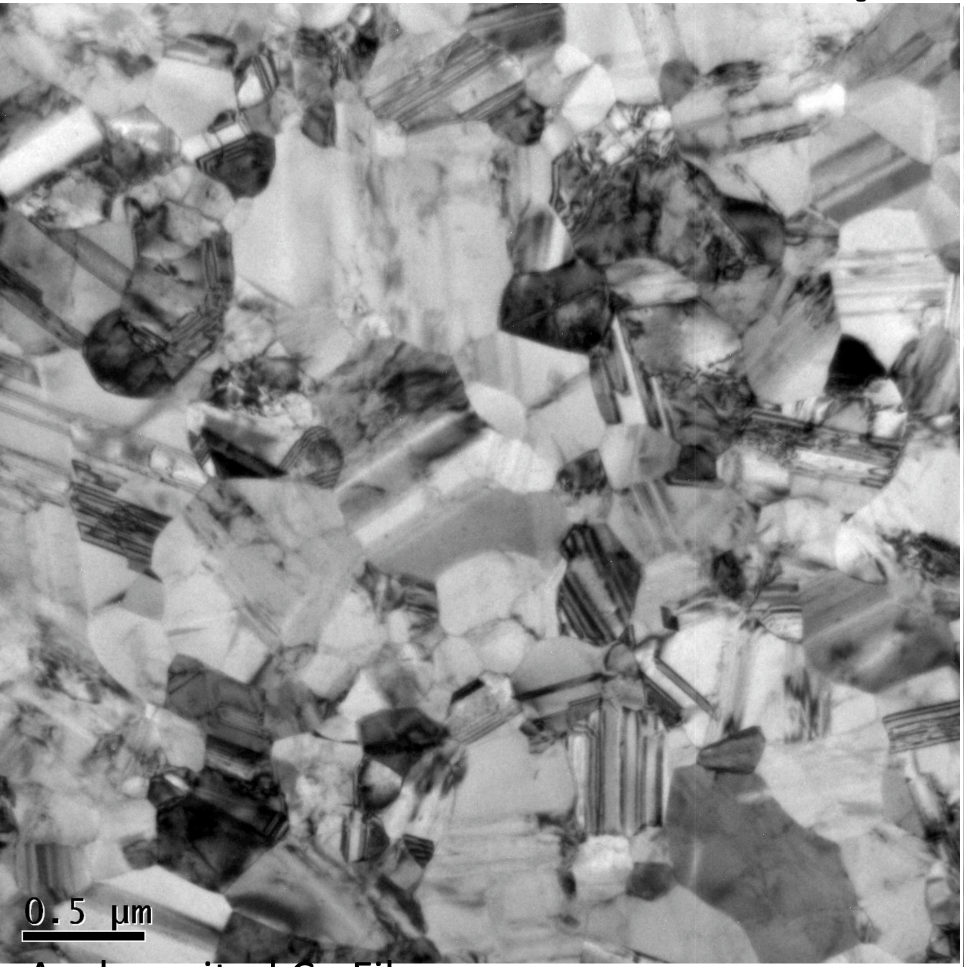
Constant vs. Instantaneous Diffusion Source



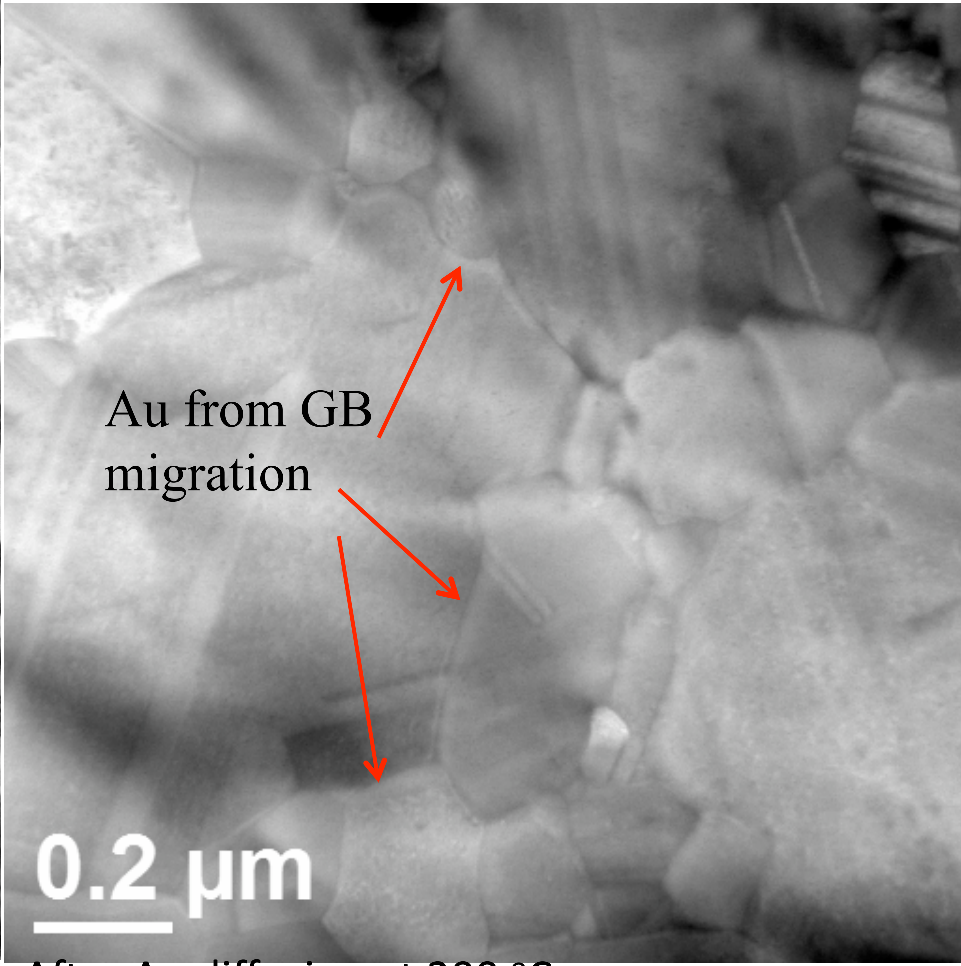
Au diffusion in As-deposited Cu



As-Deposited Cu



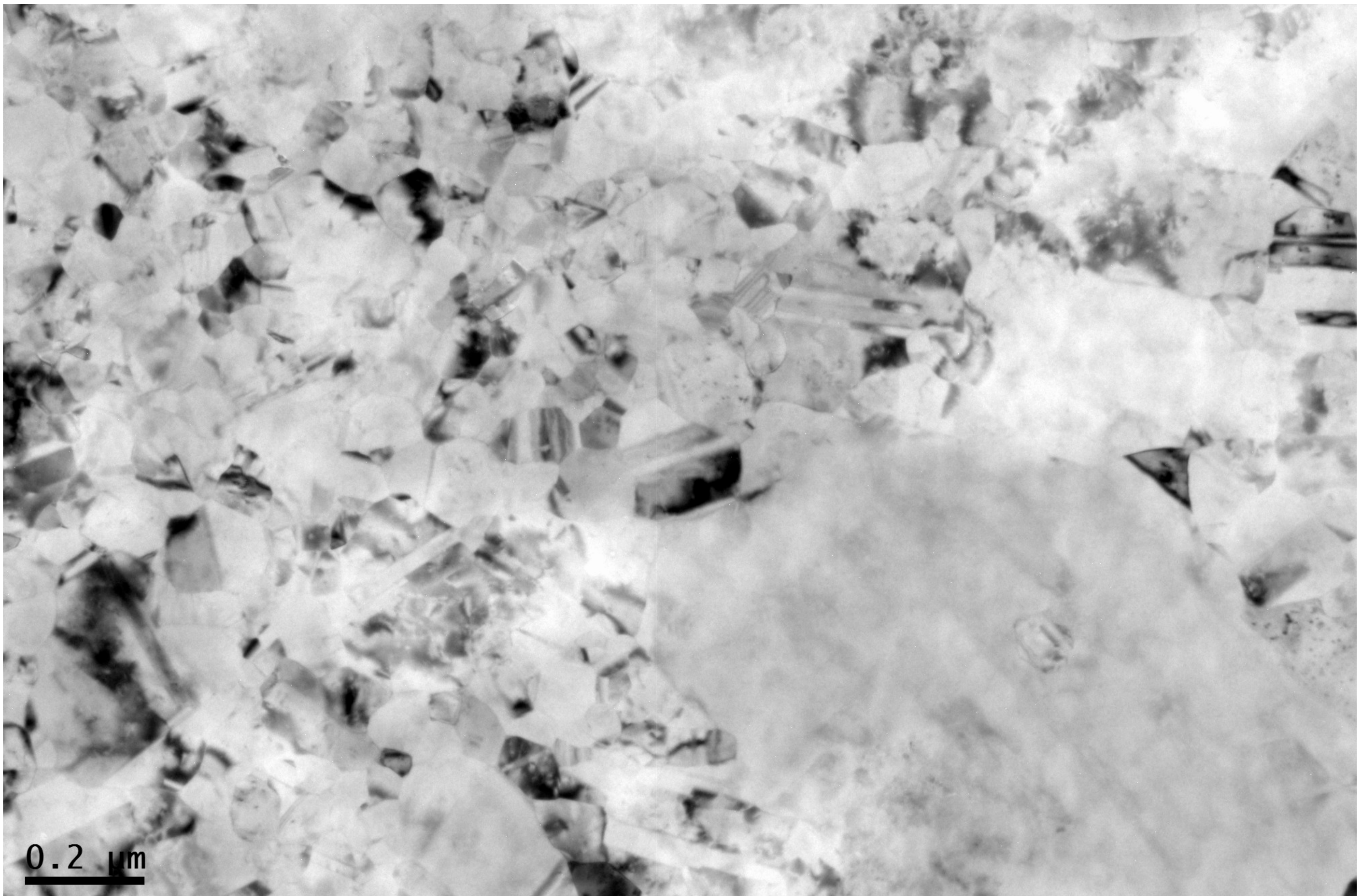
As deposited Cu Film



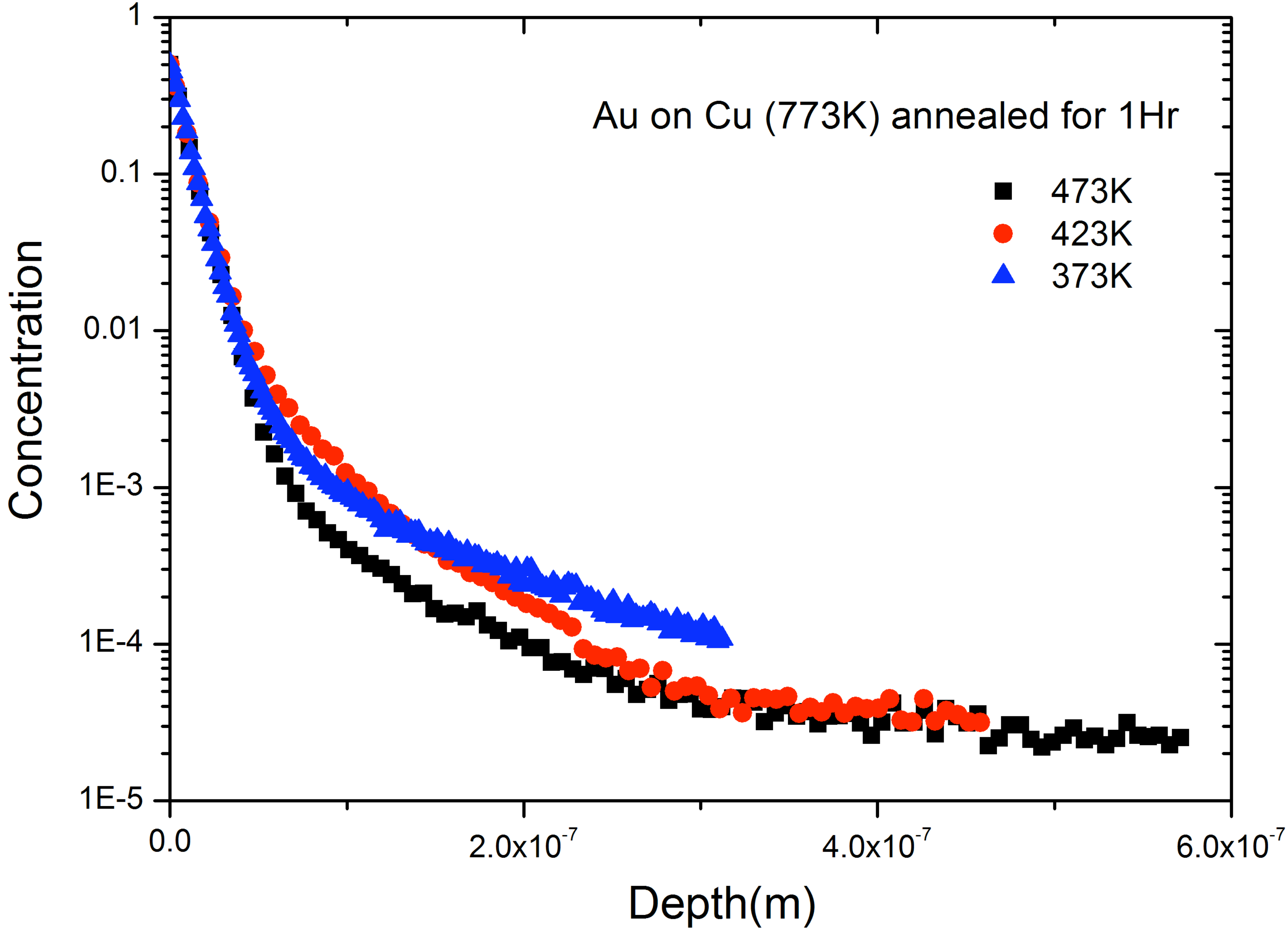
After Au diffusion at 200 ^oC

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

450 ^{o}C Abnormal Grain Growth

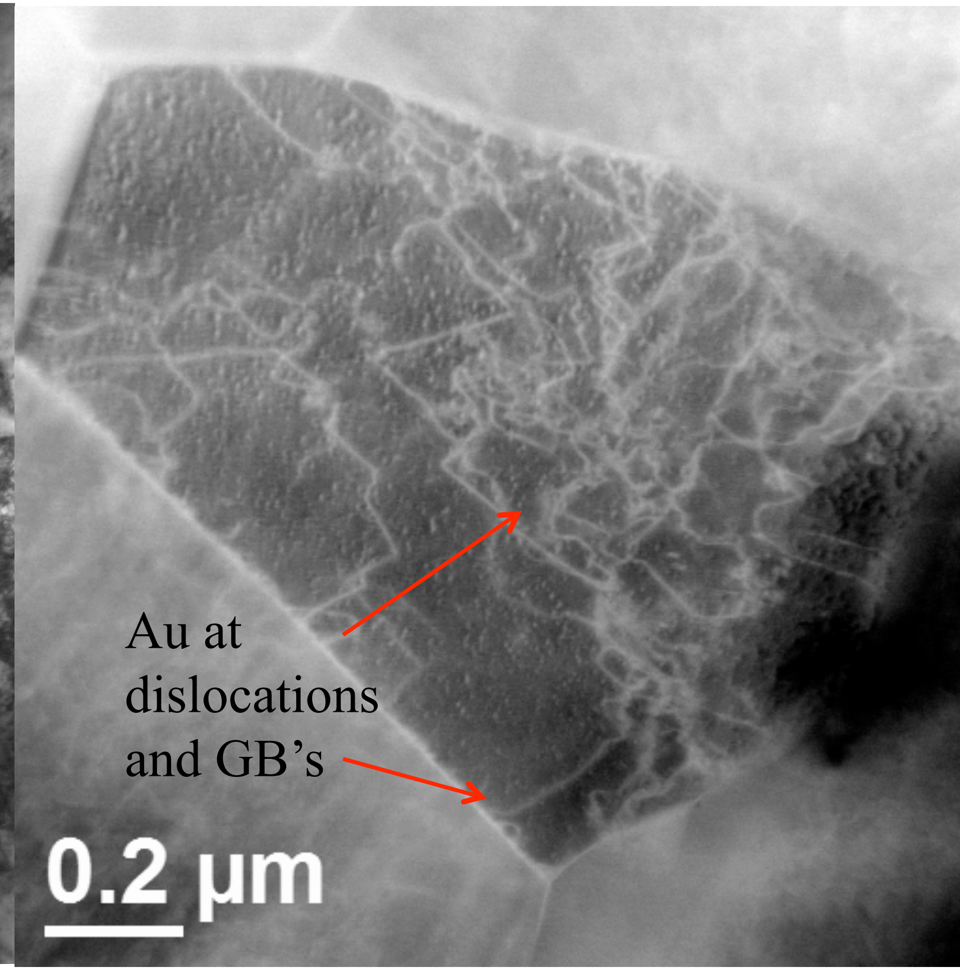


Au Diffusion in 500 ºC Annealed Cu



500 ^{o}C Annealed Cu

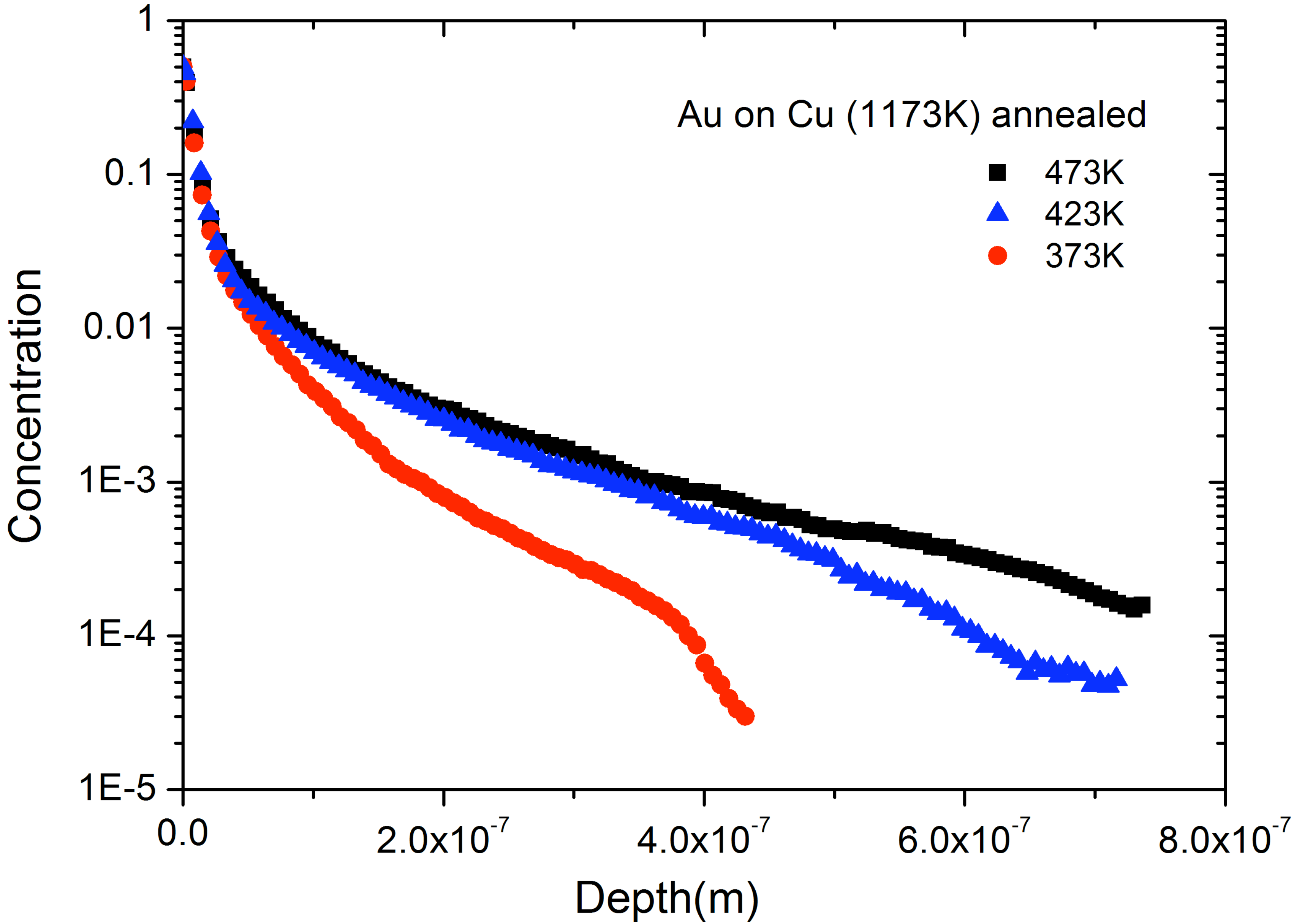
Pure Cu 500 ^{o}C pre-annealed



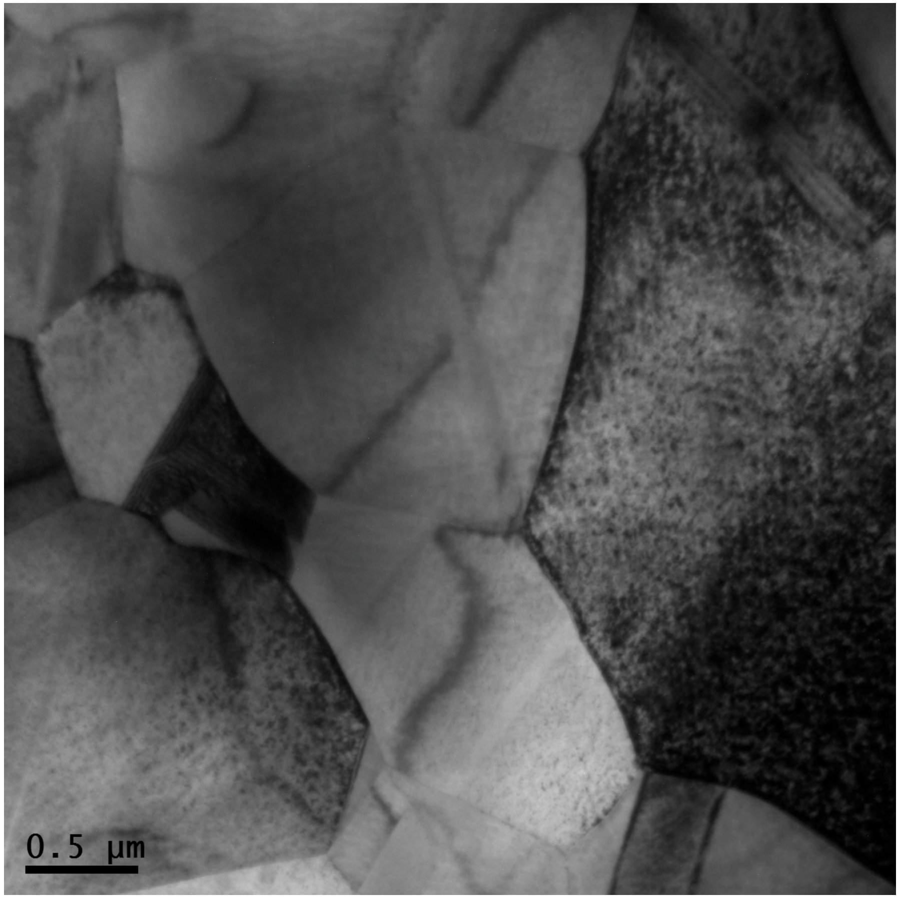
Pure Cu 500 ^{o}C pre-annealed + Au diffusion (200 ^{o}C)

No Model for G.B. Diffusion

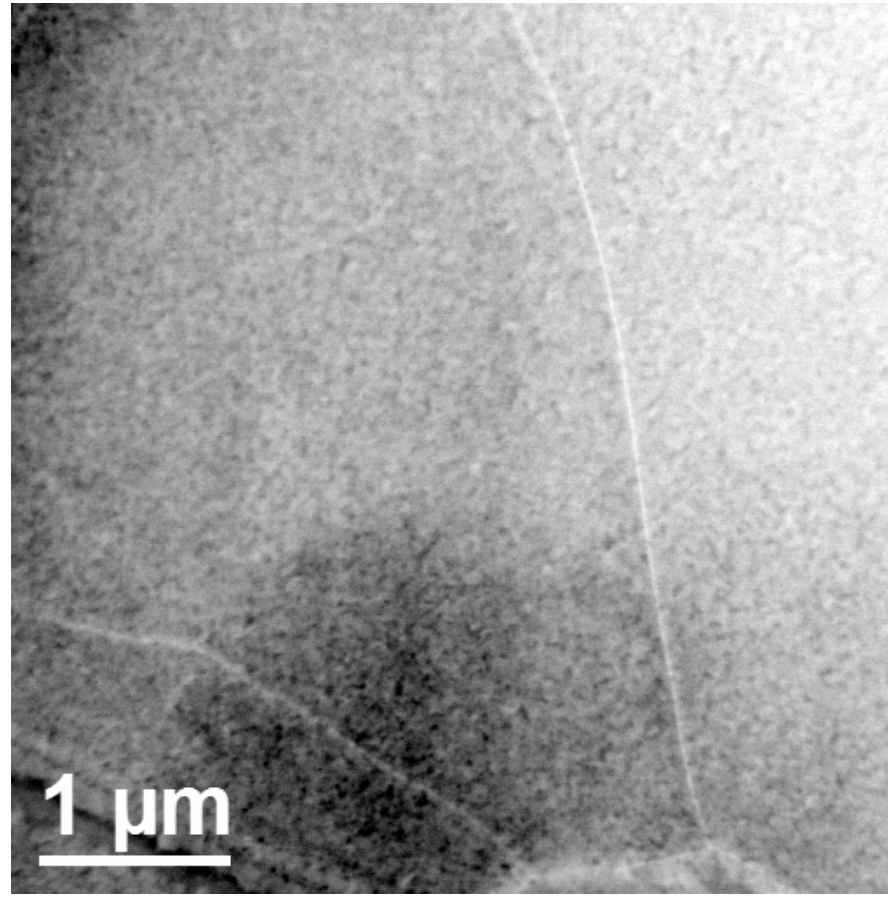
Au Diffusion in 900 °C Annealed Cu



900 ^{o}C Annealed Cu



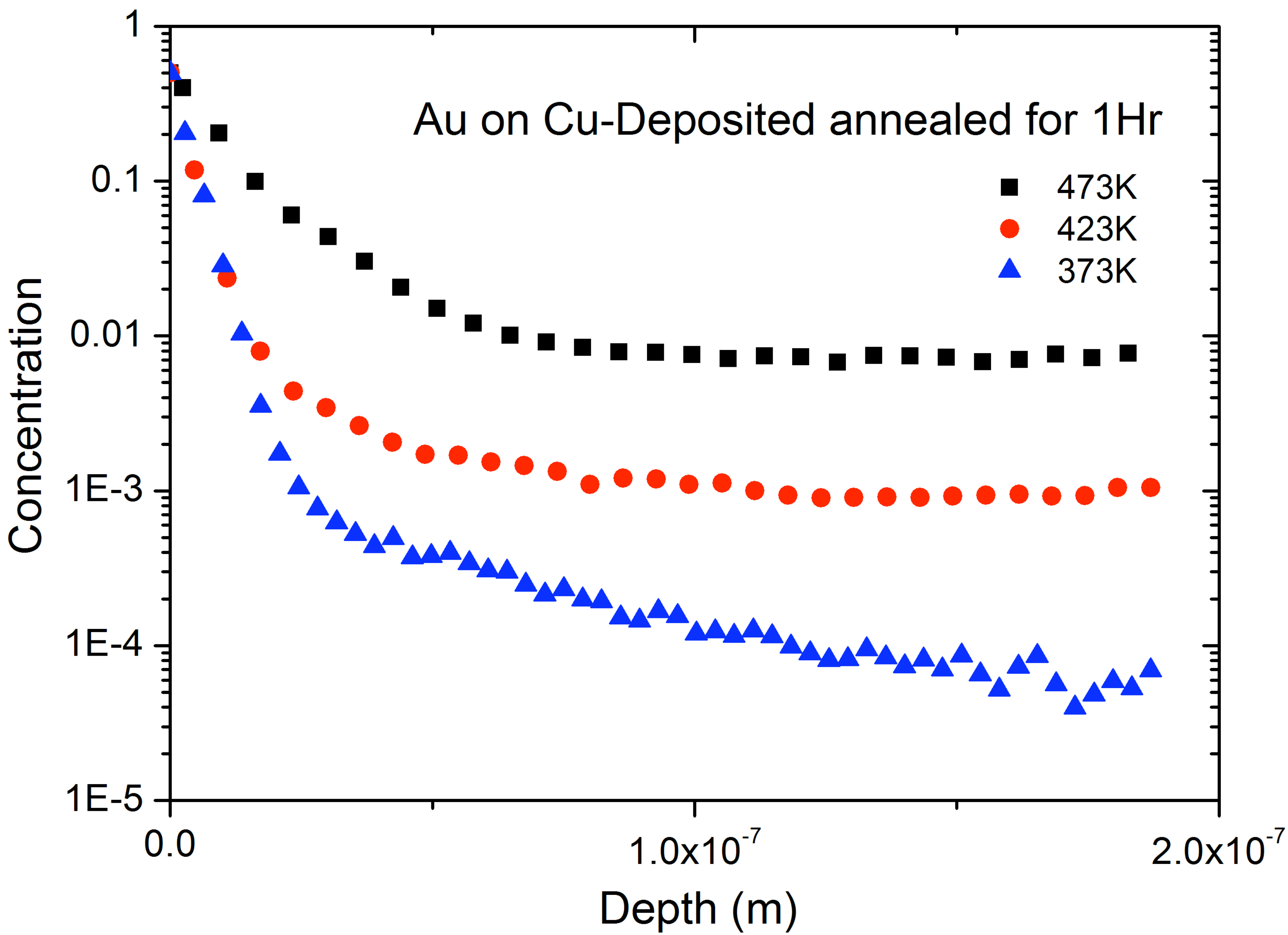
Pure Cu 900 ^{o}C pre-annealed



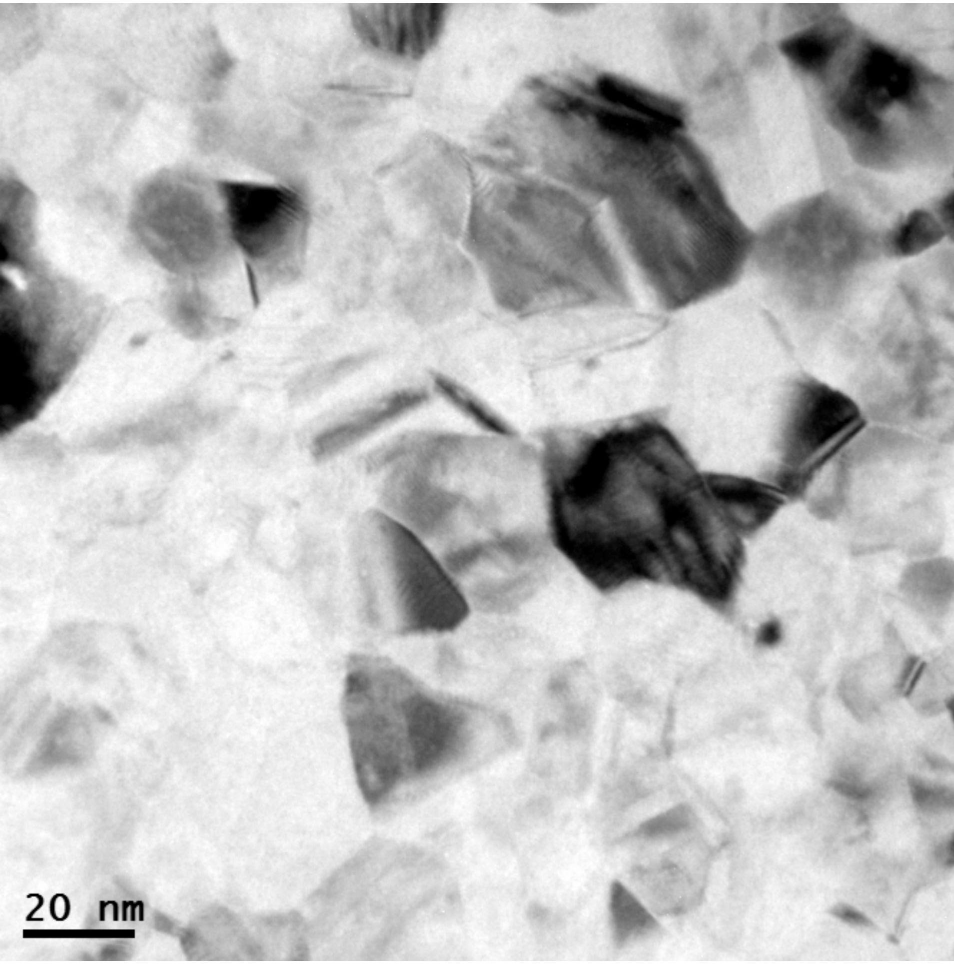
Pure Cu 900 ^{o}C pre-annealed
+ Au diffusion (200 ^{o}C)

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

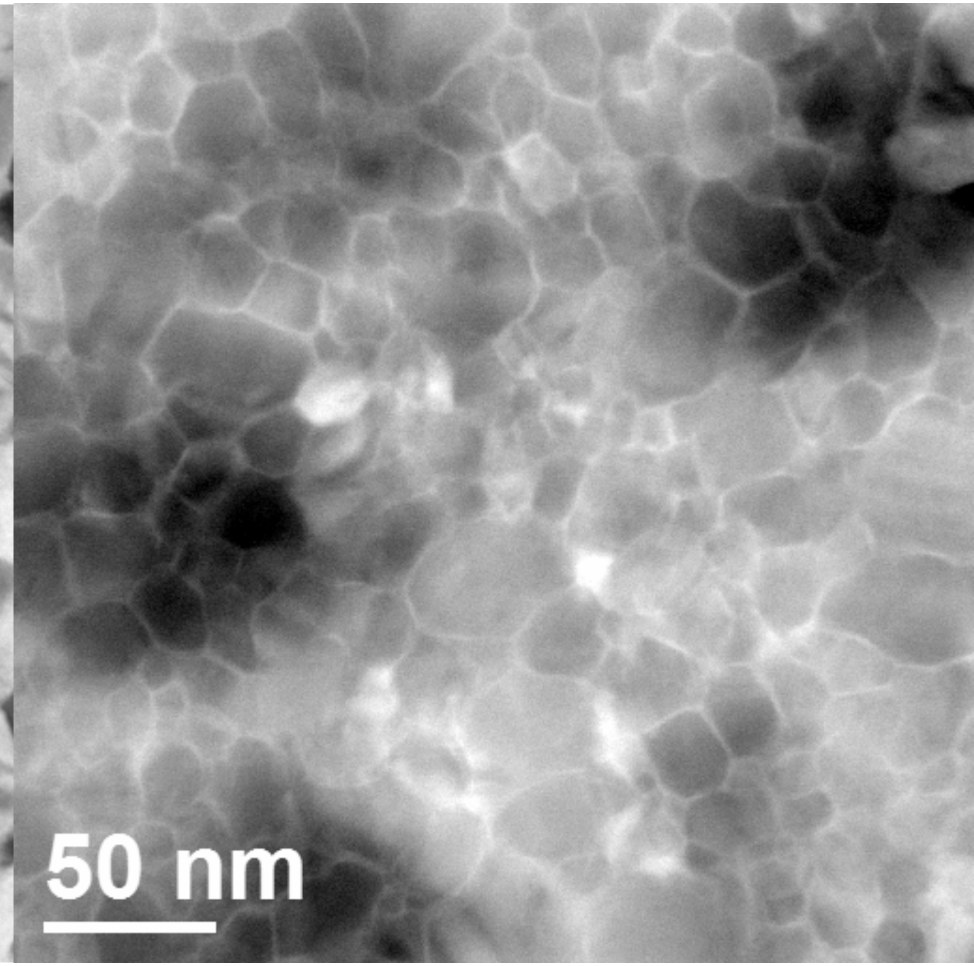
Au diffusion in 1%W-Cu As-Deposited



1%W-Cu As-Deposited

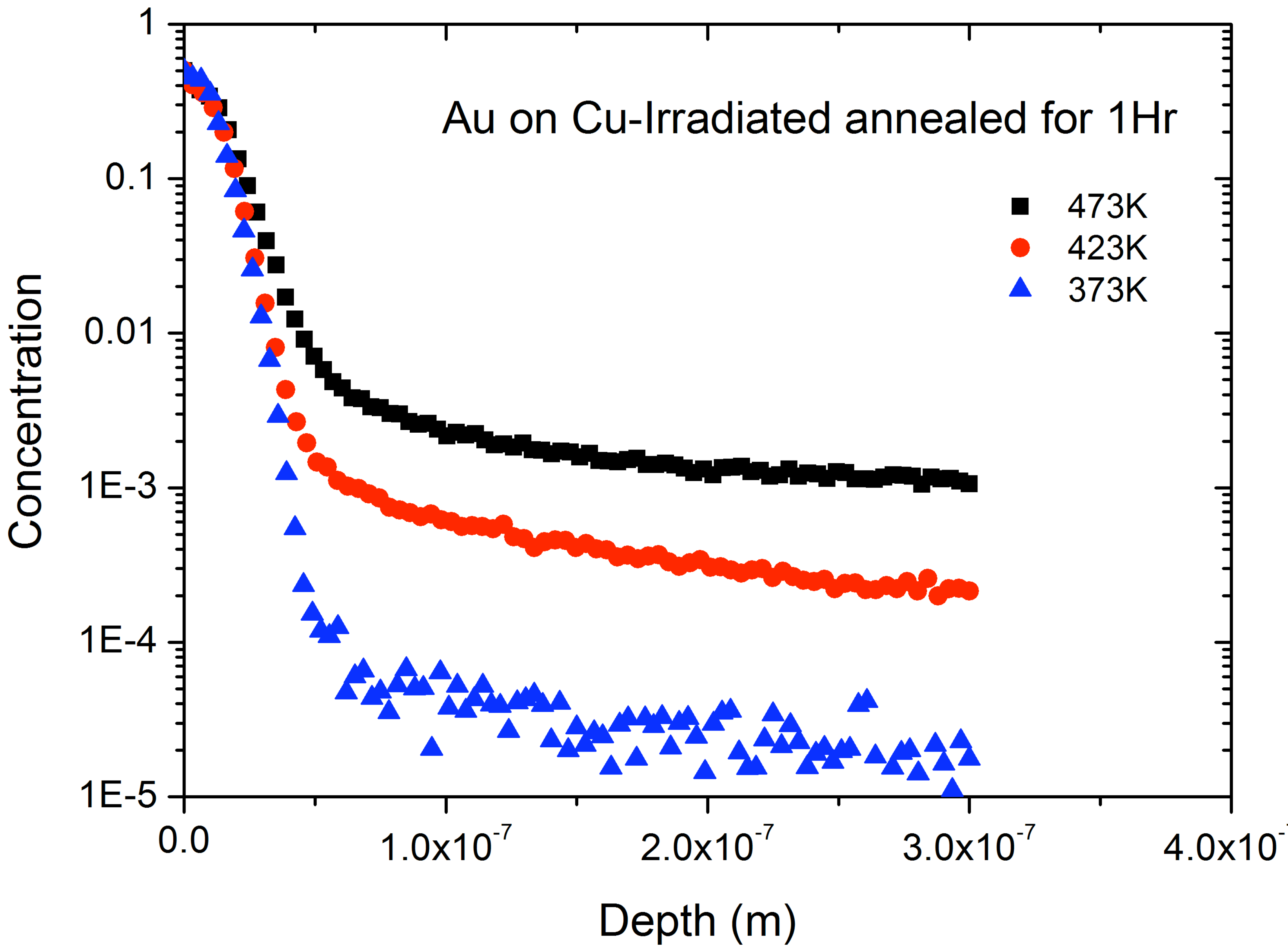


As-deposited

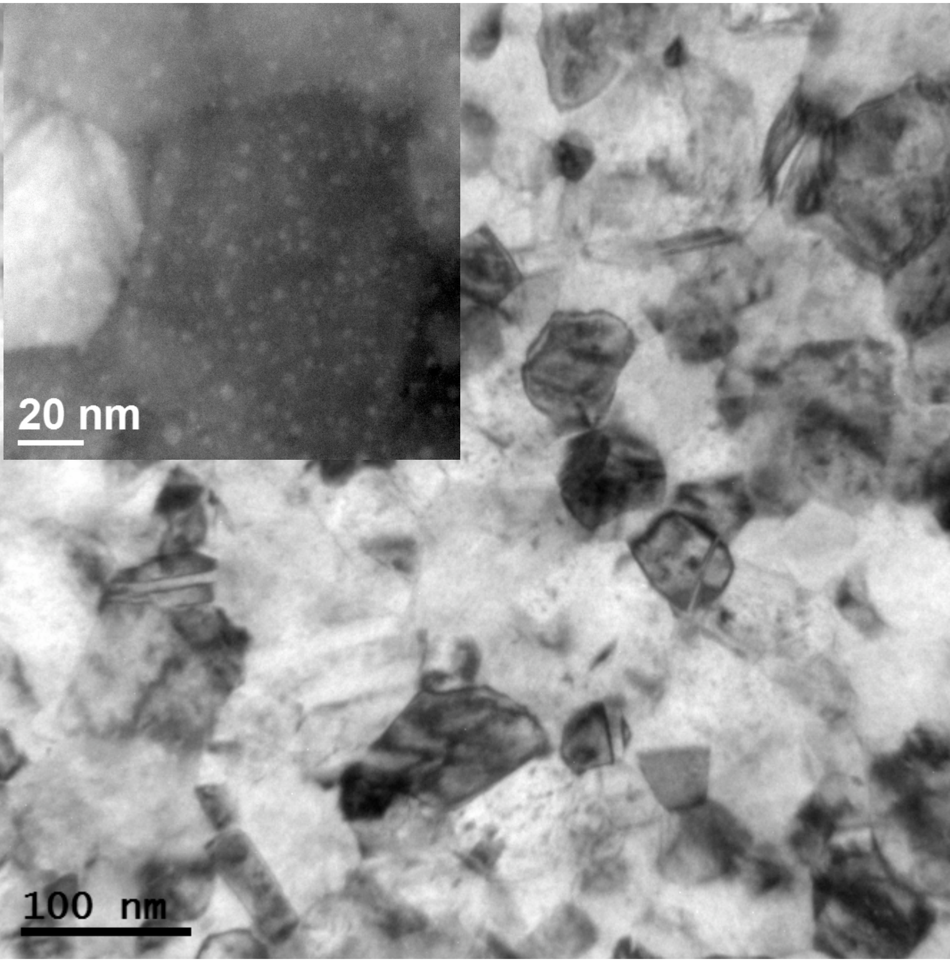


As-deposited 1%W-Cu
+ Au diffusion (200 ^{o}C)

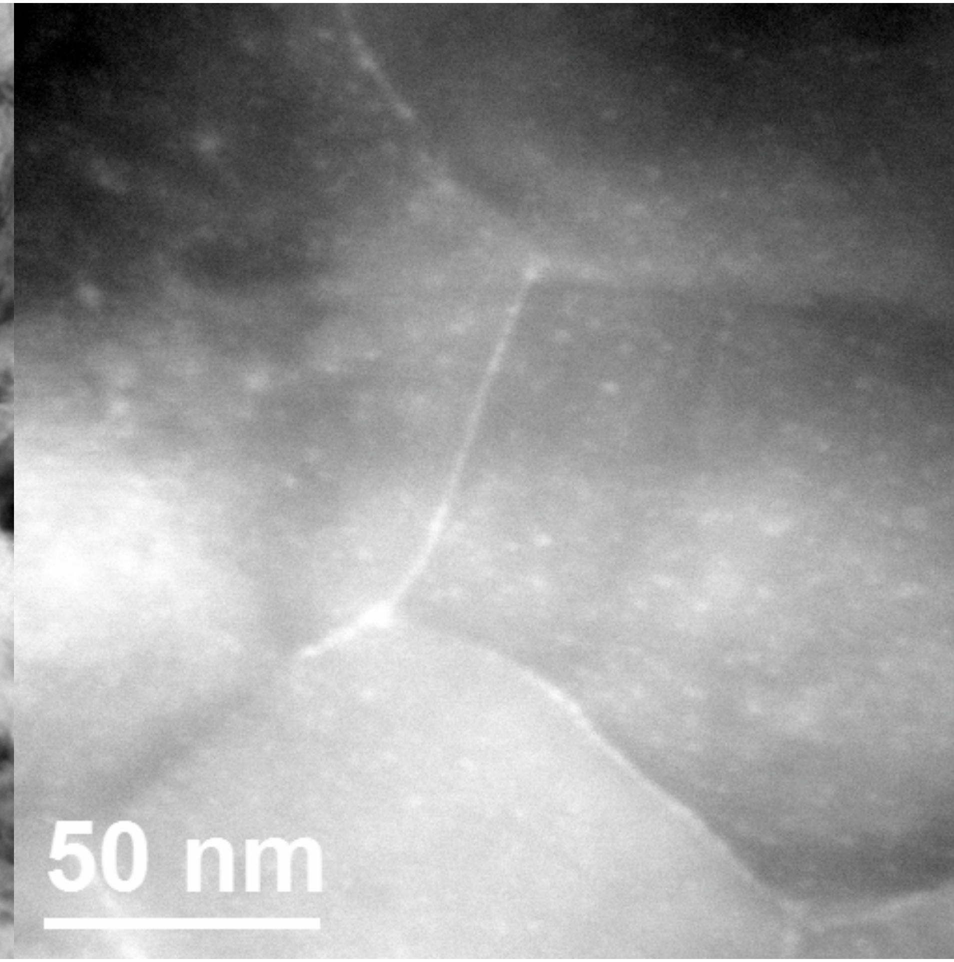
Au diffusion in 1%W-Cu Pre-Irradiated



1%W-Cu Pre-Irradiated



Irradiated



Irradiated then Au diffusion at 100 ^{o}C

Model for Equiaxed Nanograins

Type B

Constant Source

$$sD_{gb}\delta = 1.308\sqrt{\frac{D}{t}}(-\partial\bar{c}/\partial z^{6/5})^{-5/3}$$

Modified ‘Type B’ Model

Constant Source

$$D_{gb}\delta = 1.308\sqrt{\frac{D^{eff}J}{t}}\left(-\partial\bar{c}/\partial z^{6/5}\right)^{-5/3}$$

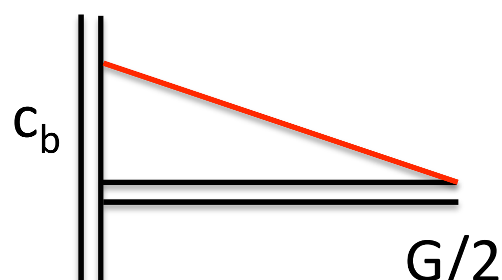
Correction Factor, J

Motivation – Basis of Type B

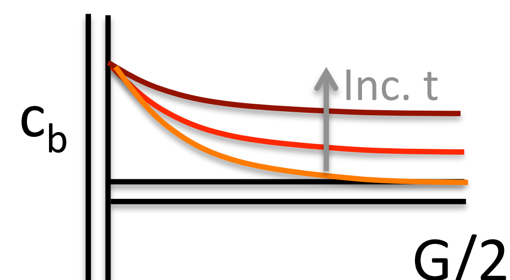
$$\frac{\partial c_b}{\partial t} = D_b\frac{\partial^2 c_b}{\partial x^2} - J\frac{2D}{\delta}\frac{\partial c_g}{\partial r}\bigg|_{r=r_b}$$

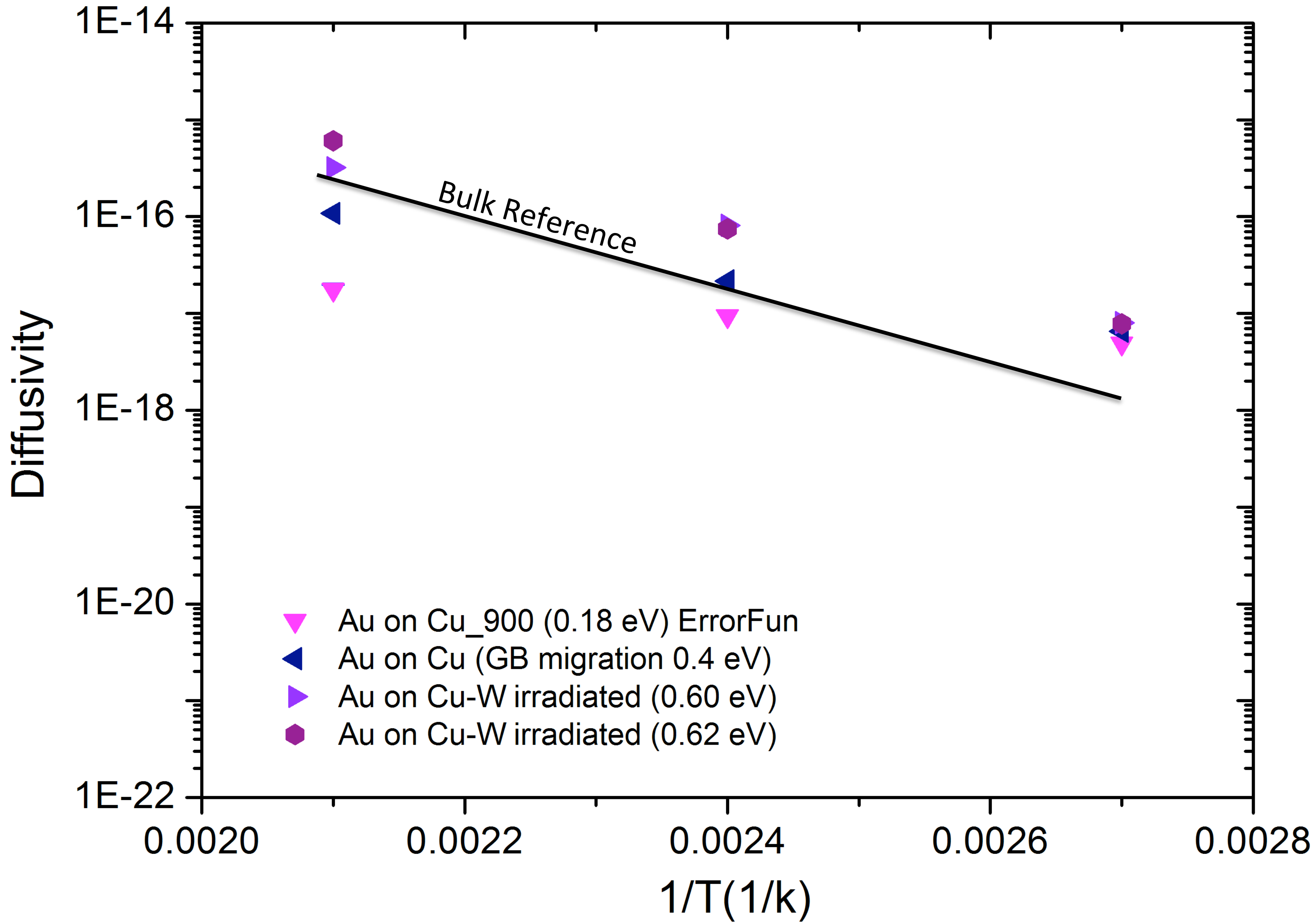
$$J = \frac{\int D\left(\partial c/\partial x\right)dt}{\int D\left(\partial^2 c/\partial x^2\right)dt}$$

$\partial c/\partial t = D\left(\partial c/\partial x\right)$



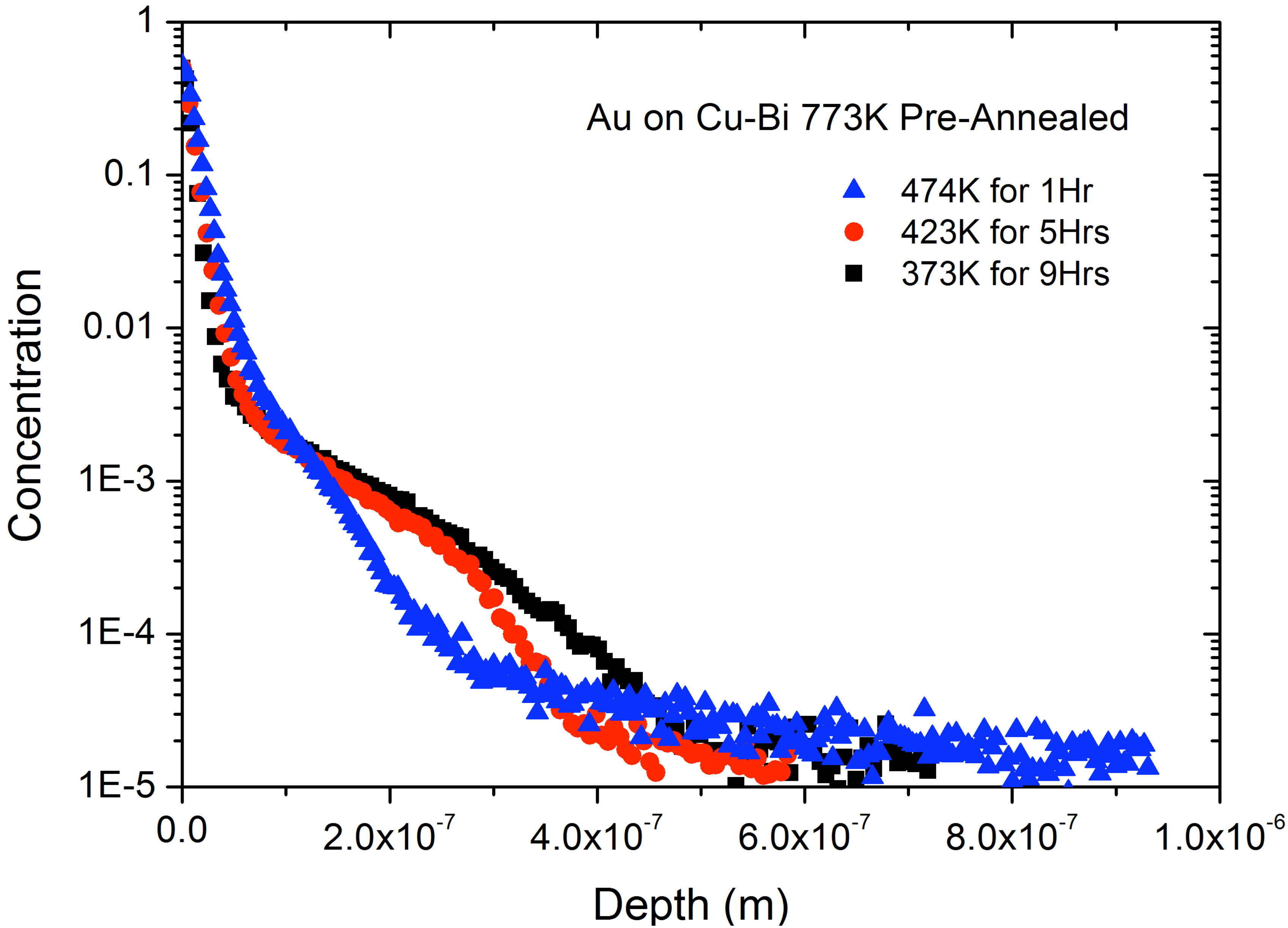
$\partial c/\partial t = D\left(\partial^2 c/\partial x^2\right)$



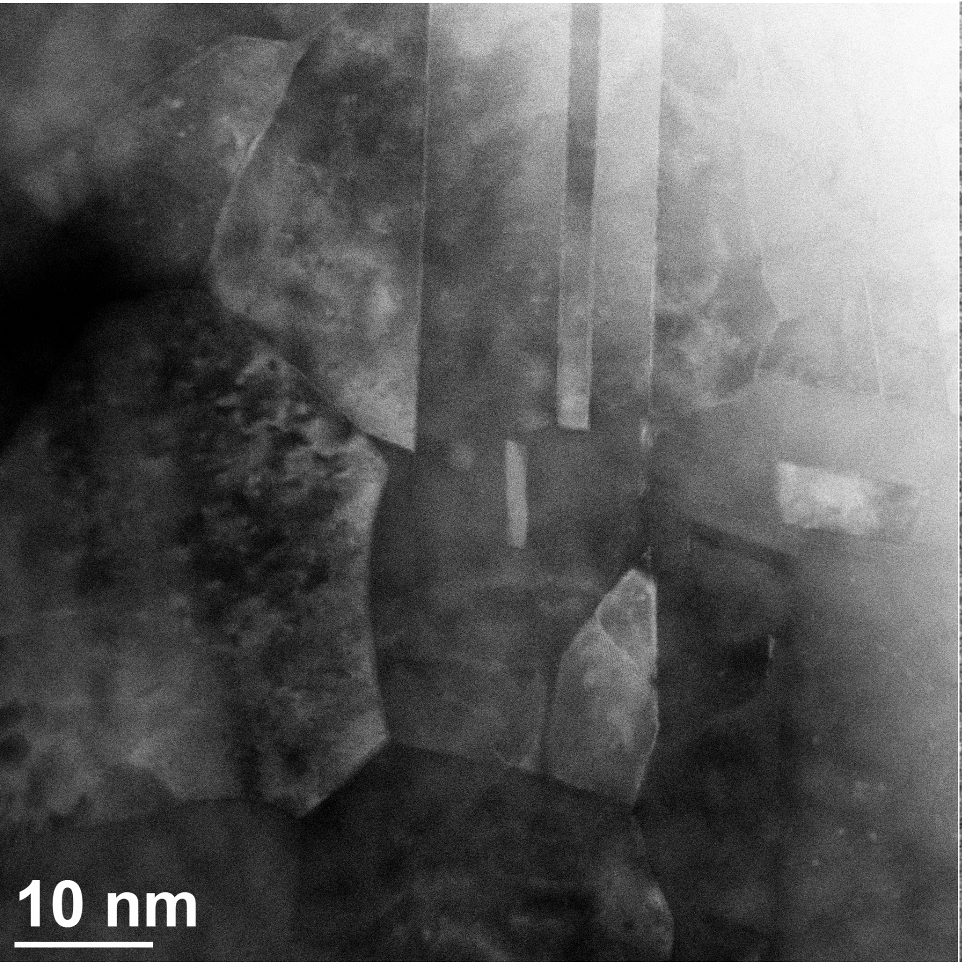


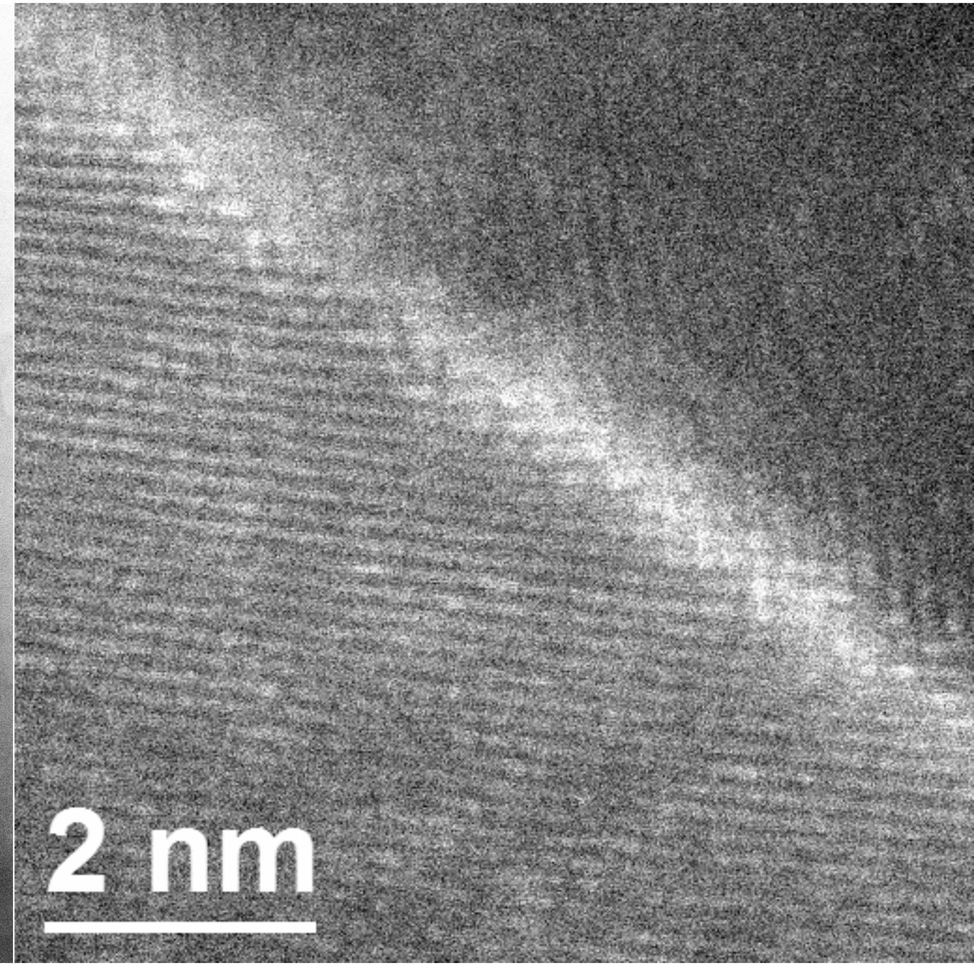
Au diffusivity in the Cu – No significant 'nano-effect'

Au Diffusion in Cu-Bi 500 °C Pre-Annealed

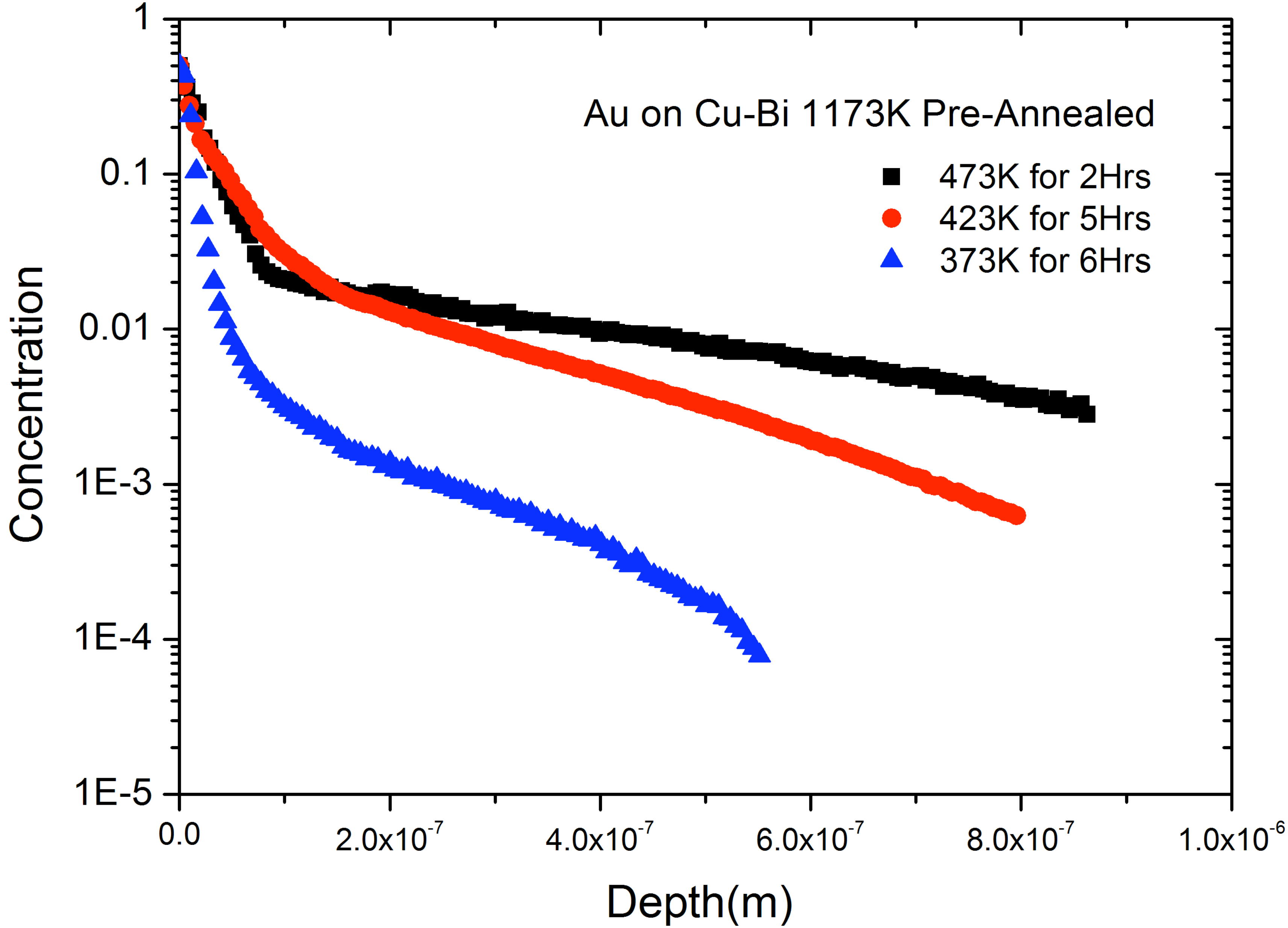


500 ºC Pre-annealed with Bi

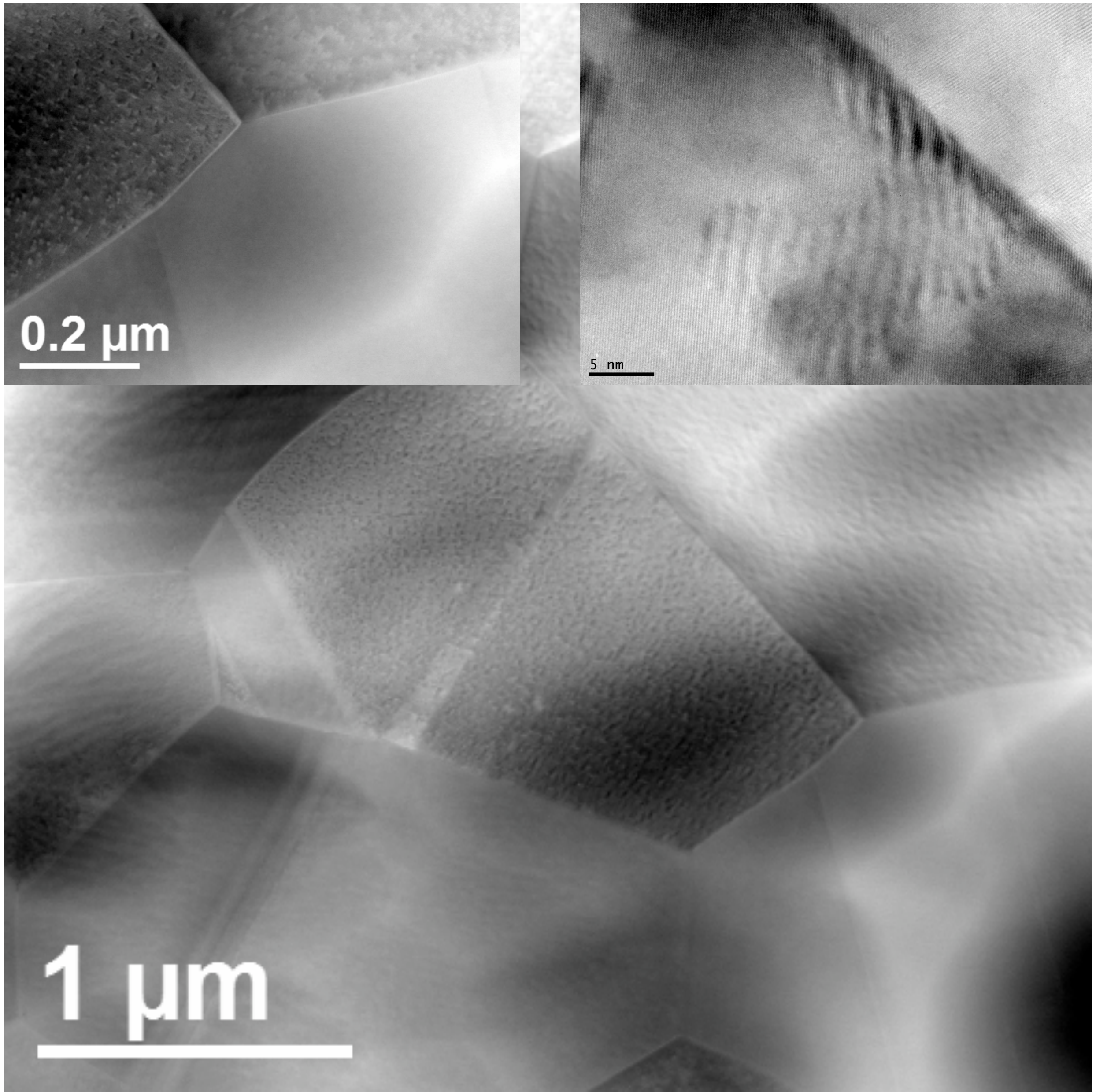


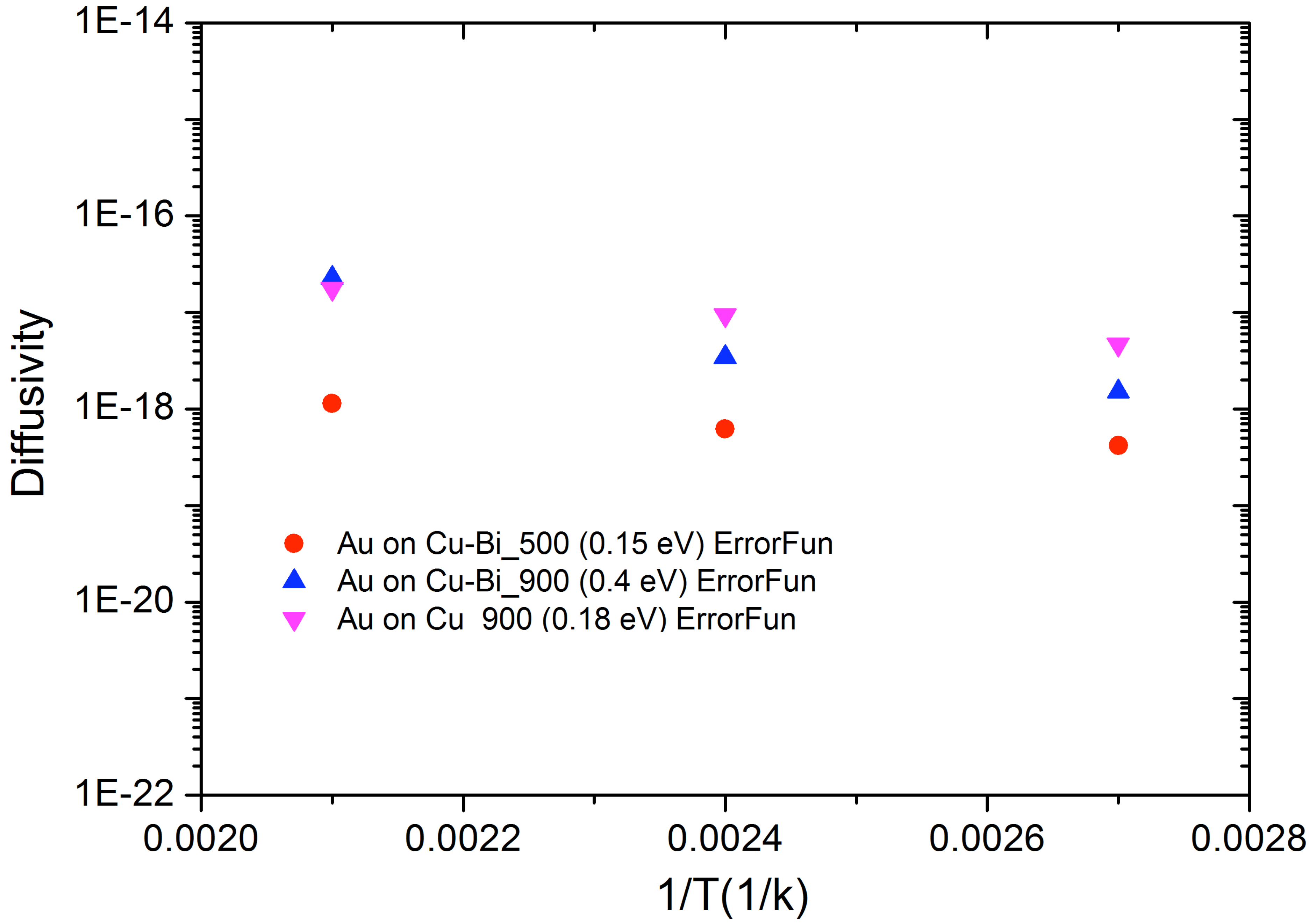


Au Diffusion in Cu-Bi 900 °C Pre-Annealed



900 ^{o}C Pre-annealed with Bi





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

Conclusions and Future Work

- No Significant ‘nano-effect’ or ‘G.B. relaxation’
- Effect of Bi on G.B. diffusion consistent with what might be expected based on alumina

- Measure Diffusivity of Cu in Ni G.B.’s
- Finish electron microscopy work
- Measure Diffusion Anisotropy??