TAILORING OF ATOMIC-SCALE INTERPHASE COMPLEXIONS FOR MECHANISM-INFORMED MATERIAL DESIGN

SIMS diffusion measurements in Cu and Cu alloys

The growing realization that grain boundaries can sustain a series of phases (interphases) in their own right (called interphase complexions, ICs or complexions), which are only a few atomic layers thick and which can undergo a variety of coupled structural and chemical transitions ((i.e., IC transitions)

The excitement of this discovery is the promise to design and match the type of IC structure to the demands of different applications, since indications are that the properties are highly sensitive to the IC type.

The availability of new instrumentation, such as the latest generation of high resolution aberration corrected scanning transmission electron microscopes, makes it possible to resolve and directly observe for the first time the atomic structures of ICs.

The kinetics of grain boundary diffusion will clearly be highly sensitive to the grain boundary structure (and hence the nature of the complexions present).

Our project is to survey the transport properties of a large number of boundaries by using SIMS to map the concentration of a diffusing species.

By comparing the penetration depth as a function of grain size, metal composition and heat-treatment, the role of complexion type in determining the grain boundary transport will be revealed.

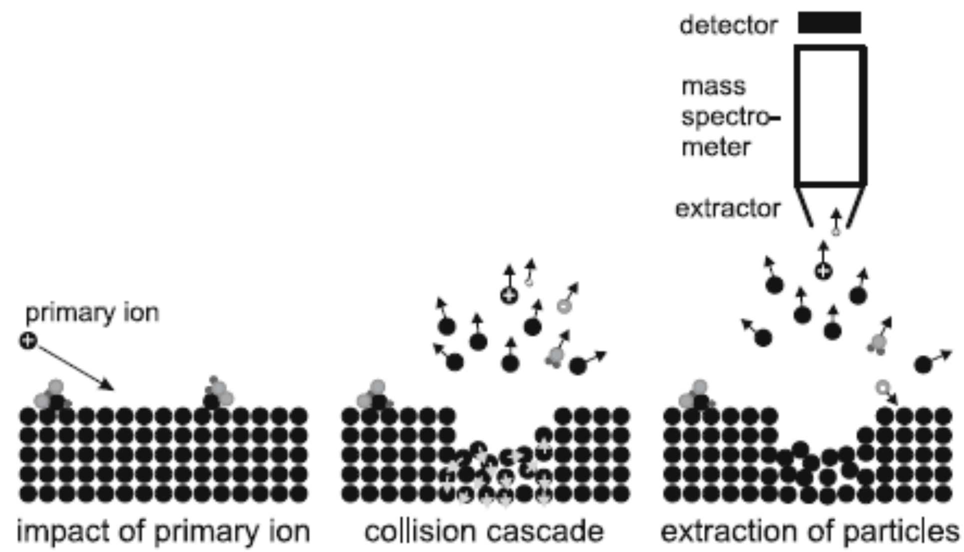
Secondary Ion Mass Spectrometry (SIMS)

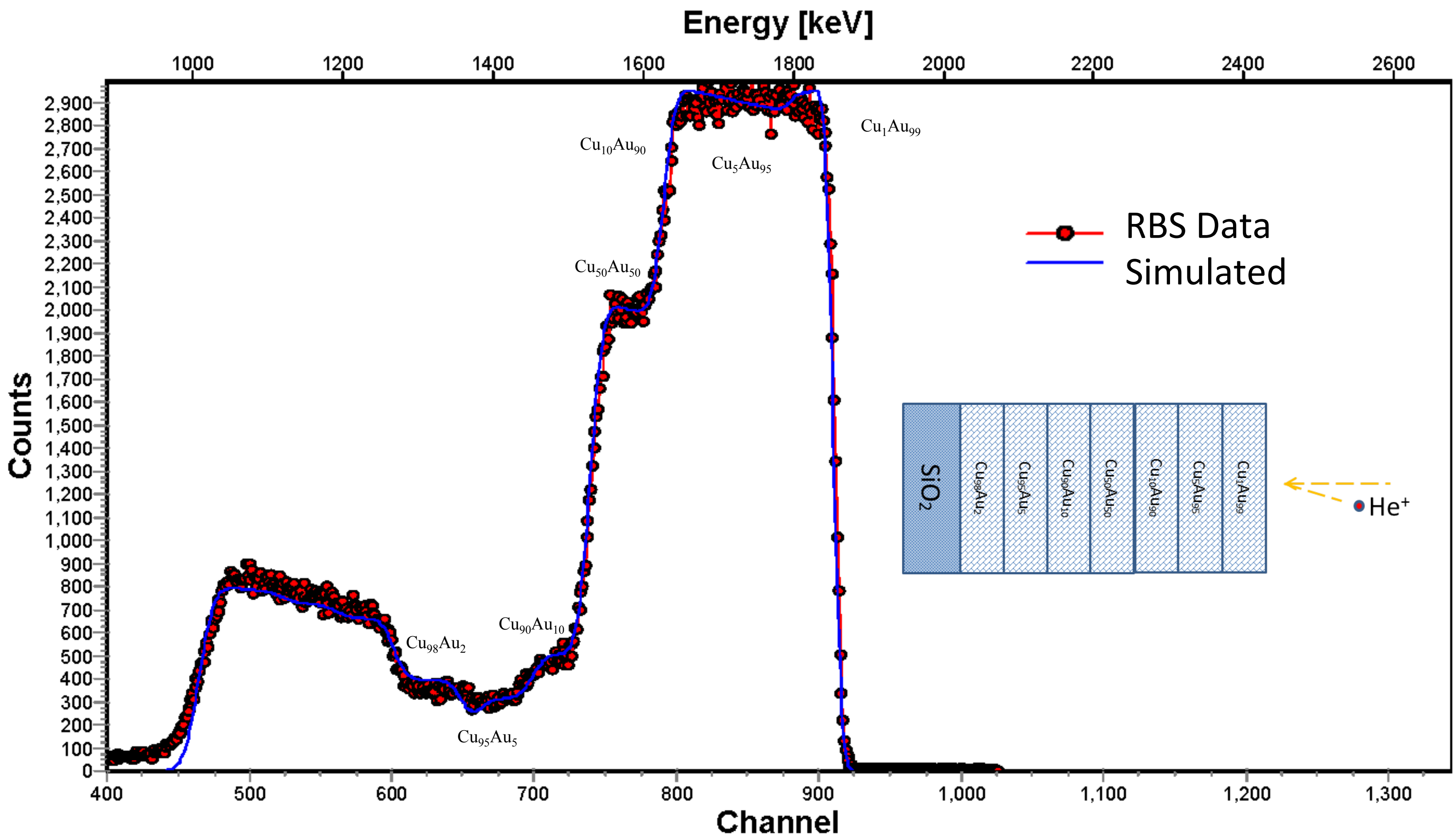
In secondary ion mass spectrometry (SIMS) a focused ion beam is directed to a solid surface, removing material in the form of neutral and ionized atoms and molecules. The secondary ions are then accelerated into a mass spectrometer and separated according to their mass-to-charge ratio. This allows for sensitivity in parts per billion for many elements and can perform depth profiles with minimum 3 nm depth resolution.

Main Problem: "Matrix Effect"

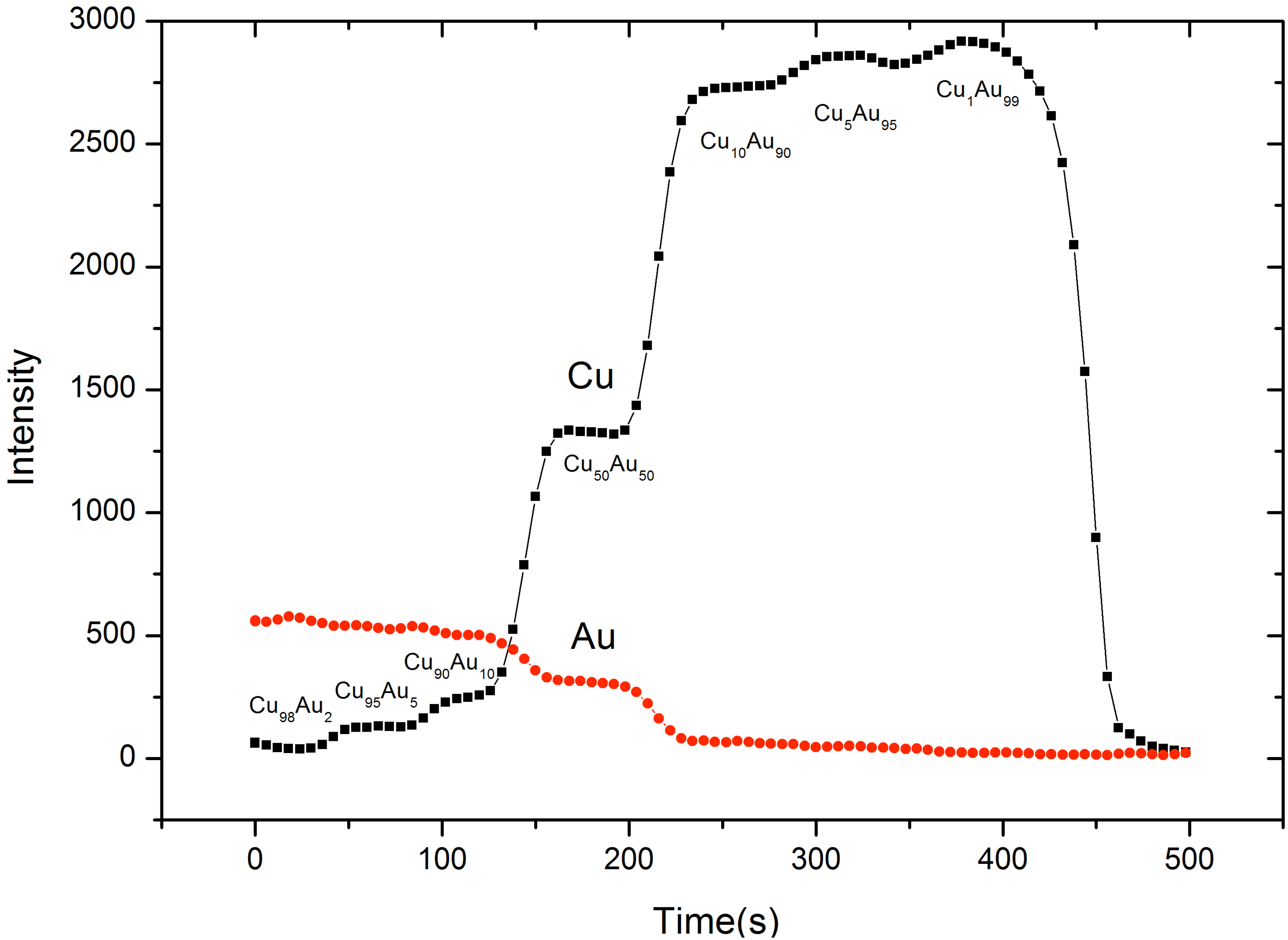
SIMS Raw Data is Count Numbers-Time and strongly depends on Chemical Environment

No "real concentration" is directly available.

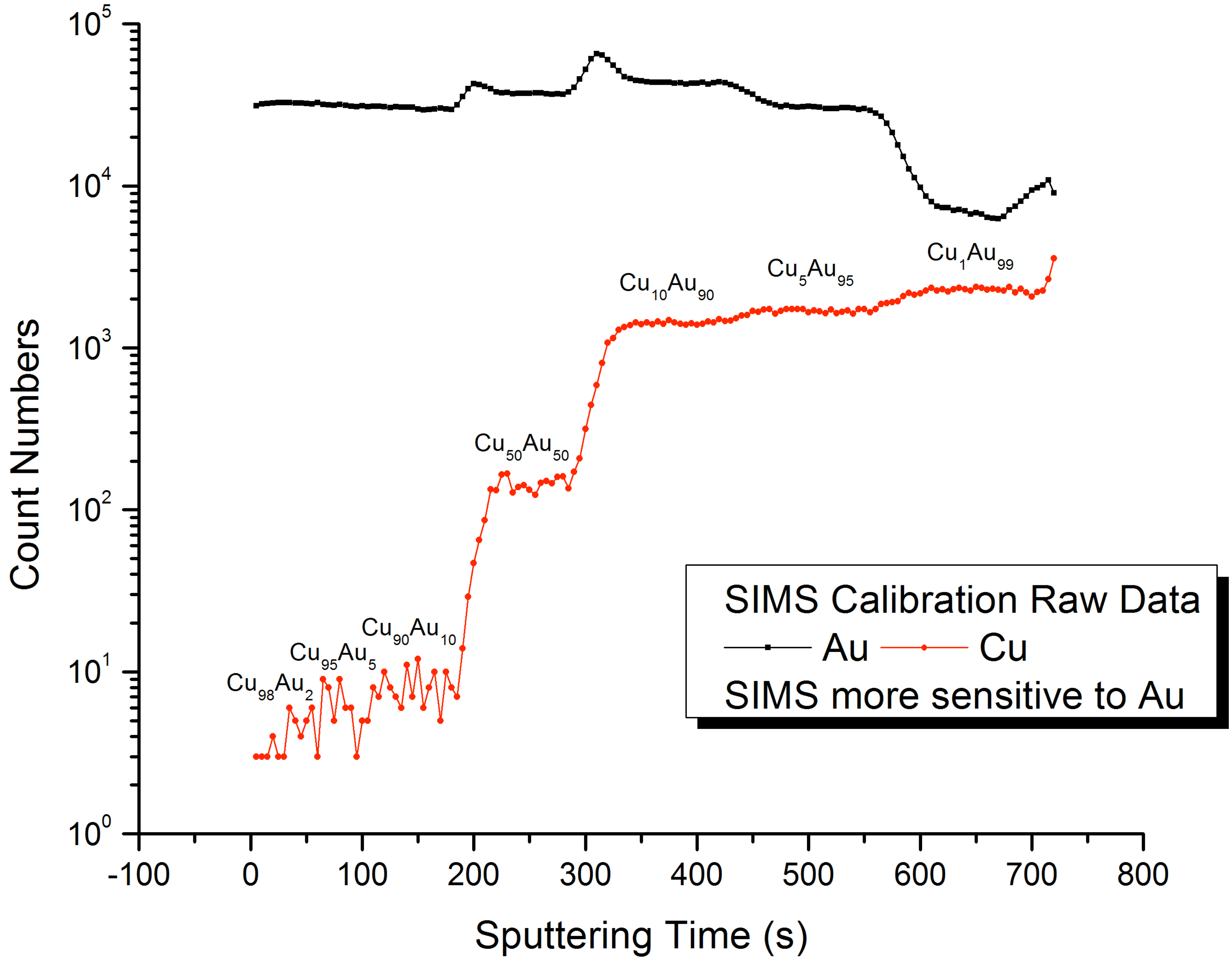




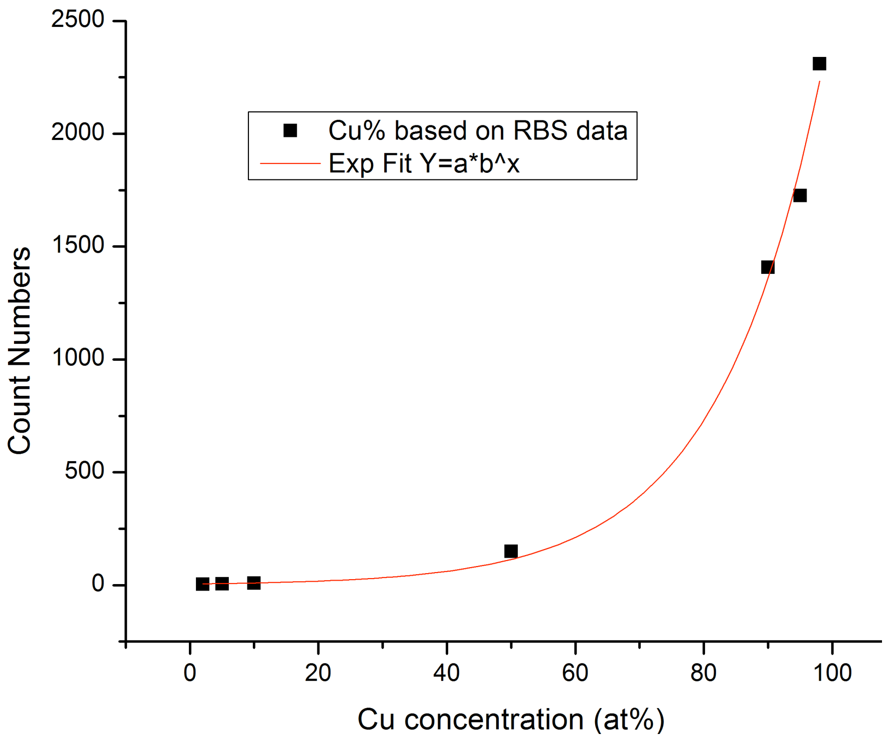
7 Multilayers Determined by RBS to Calibrate SIMS “Matrix Effect”

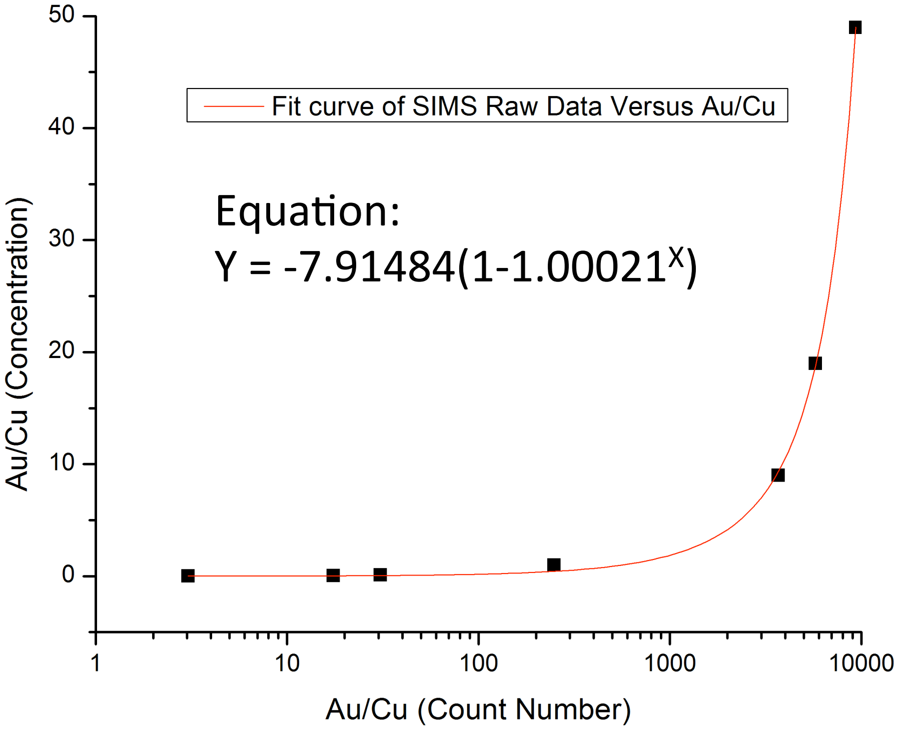


7 Multilayers Confirmed by AES (more sensitive to Cu)



7 Multilayers Determined by SIMS (more sensitive to Au)





Based on RBS and AES Results

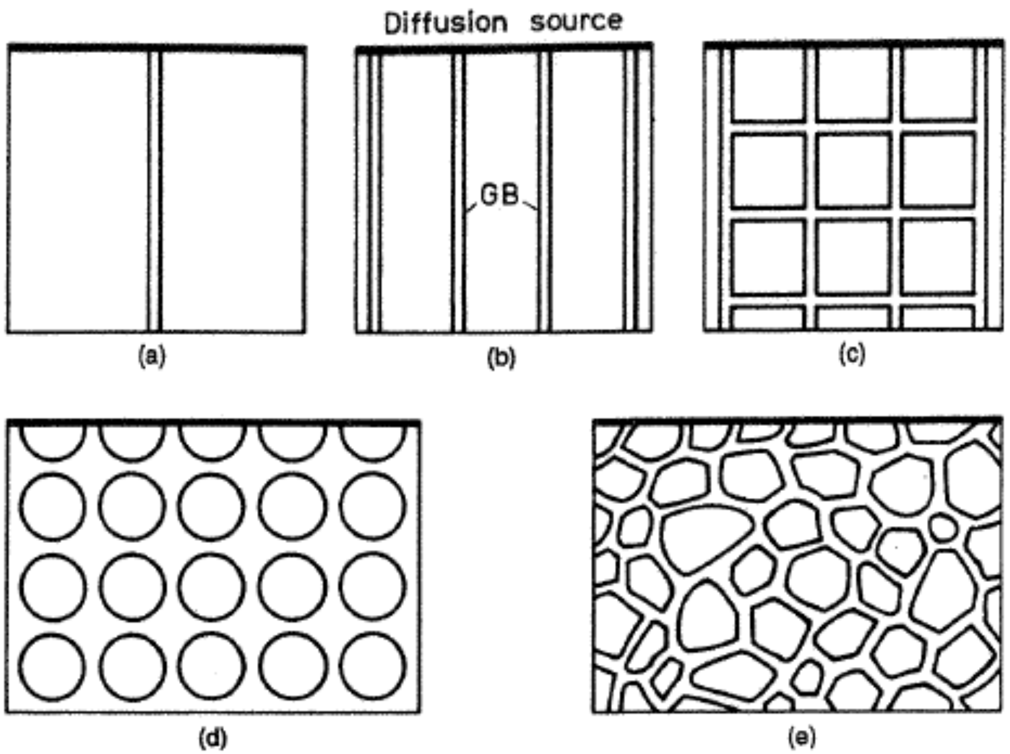
Translating SIMS Raw Data into Real Concentration is Available

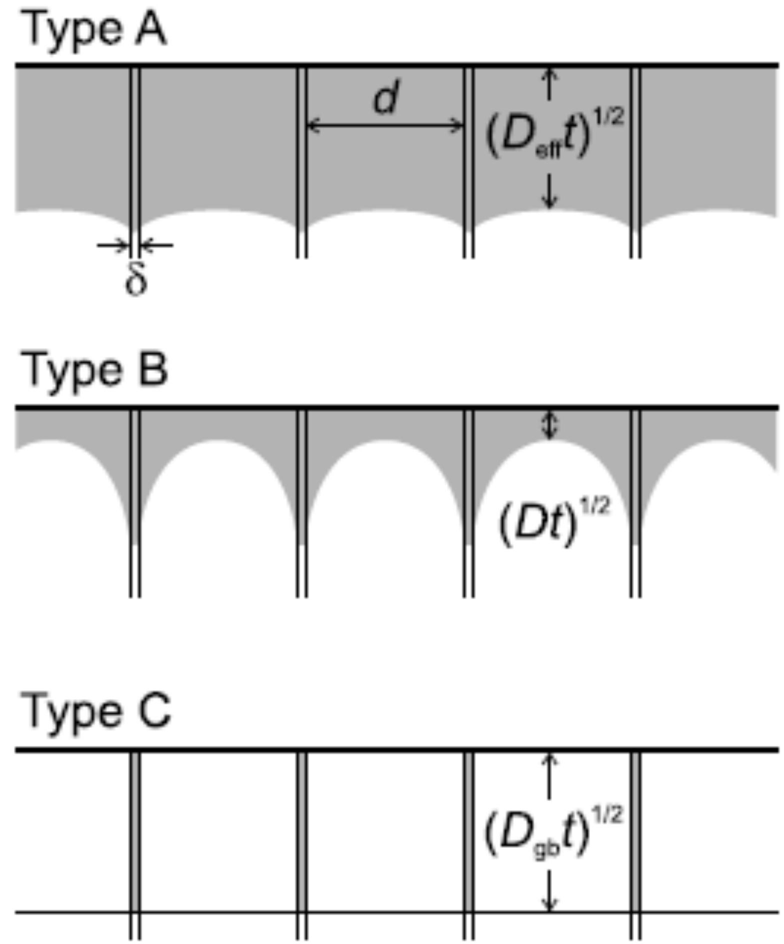
Research Work:

- Au Atoms diffusion along nano-crystal grain boundary by SIMS

Au in pure nano-crystal and micro-Cu
(grain size effect)
Au in nano-Cu-W alloy (chemical environment effect)
Au in irradiated Cu-W alloy (GB microstructure effect)
Au in Bi GB-doped Cu
Constant source experiments (have been compared w/ instantaneous source in several cases)

- Microstructures and chemical compositions by HREM, STEM, EDS





Conventional diffusion and microstructural models for bulk materials

Equations for Fitting Diffusion Data

Type B: Instantaneous Source

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

Type B: Constant Source

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

Type C: Instantaneous Source

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

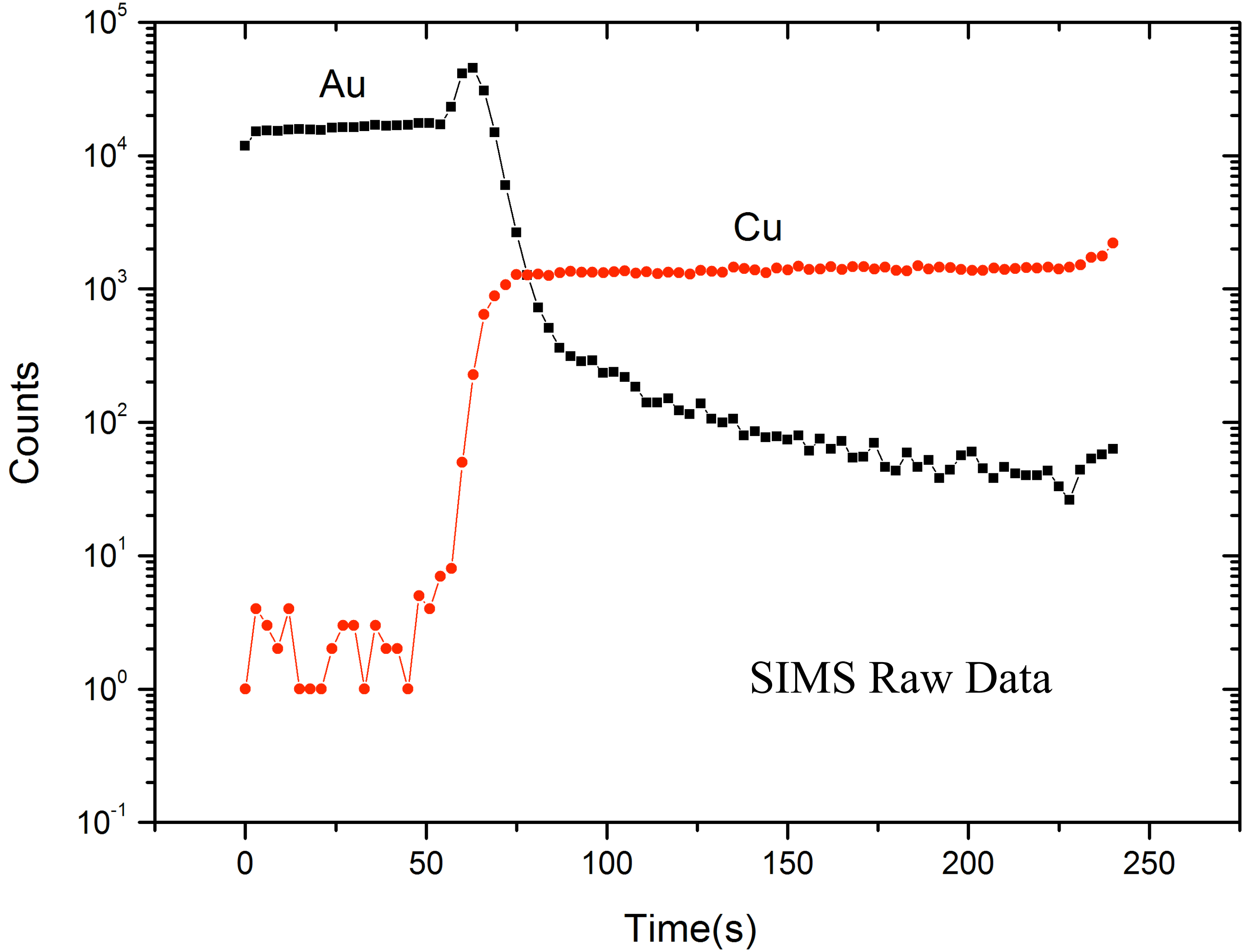
Type C: Constant Source

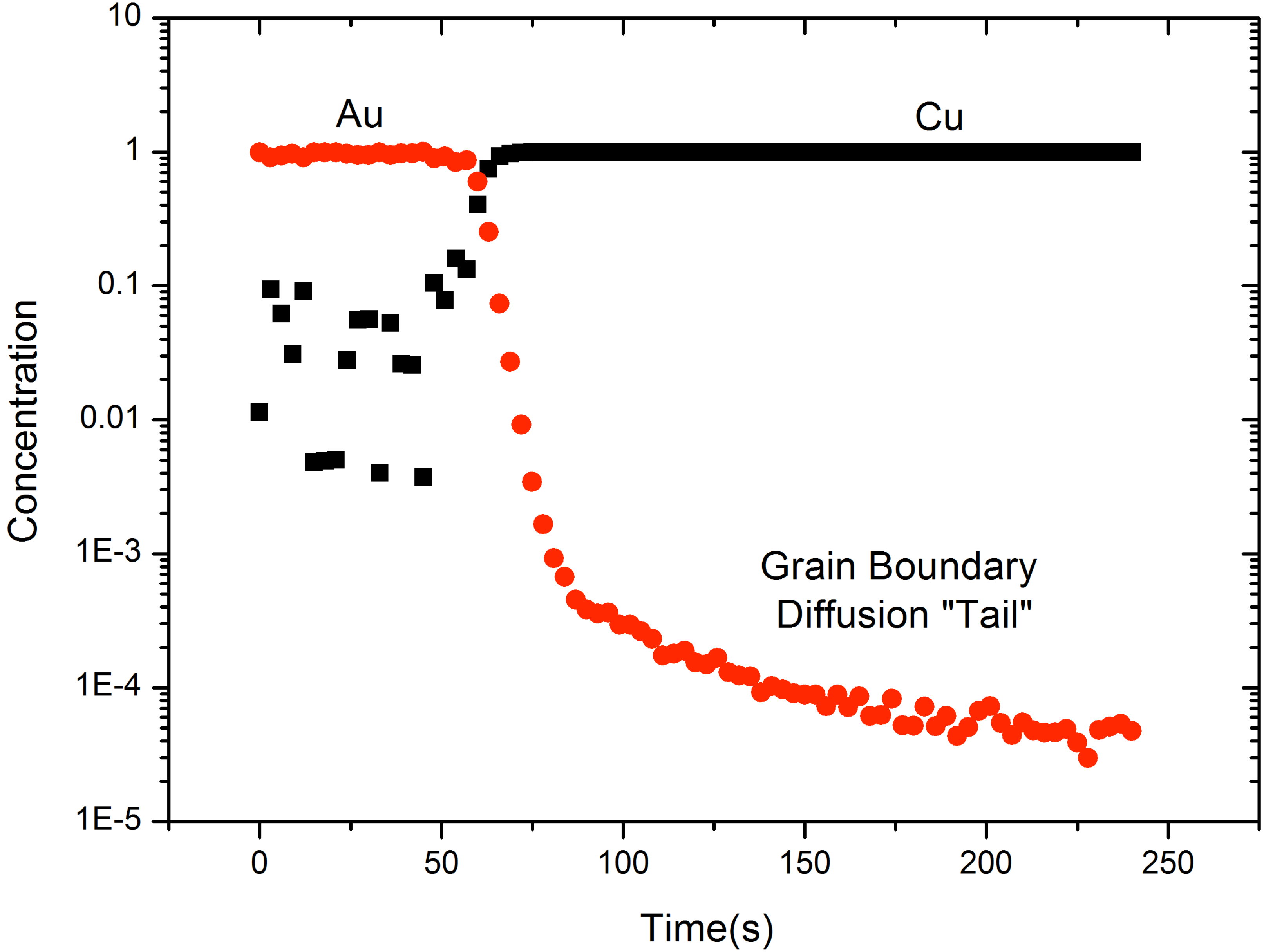
$$\bar{c}(z) \approx \bar{c}_{gb}(z) \propto \operatorname{erfc}\left(\frac{z}{2\sqrt{D_{gb}t}}\right)$$

Mobile Grain Boundaries

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

For example: Au (100nm)/Cu(200nm) Annealed at 373K 1Hr

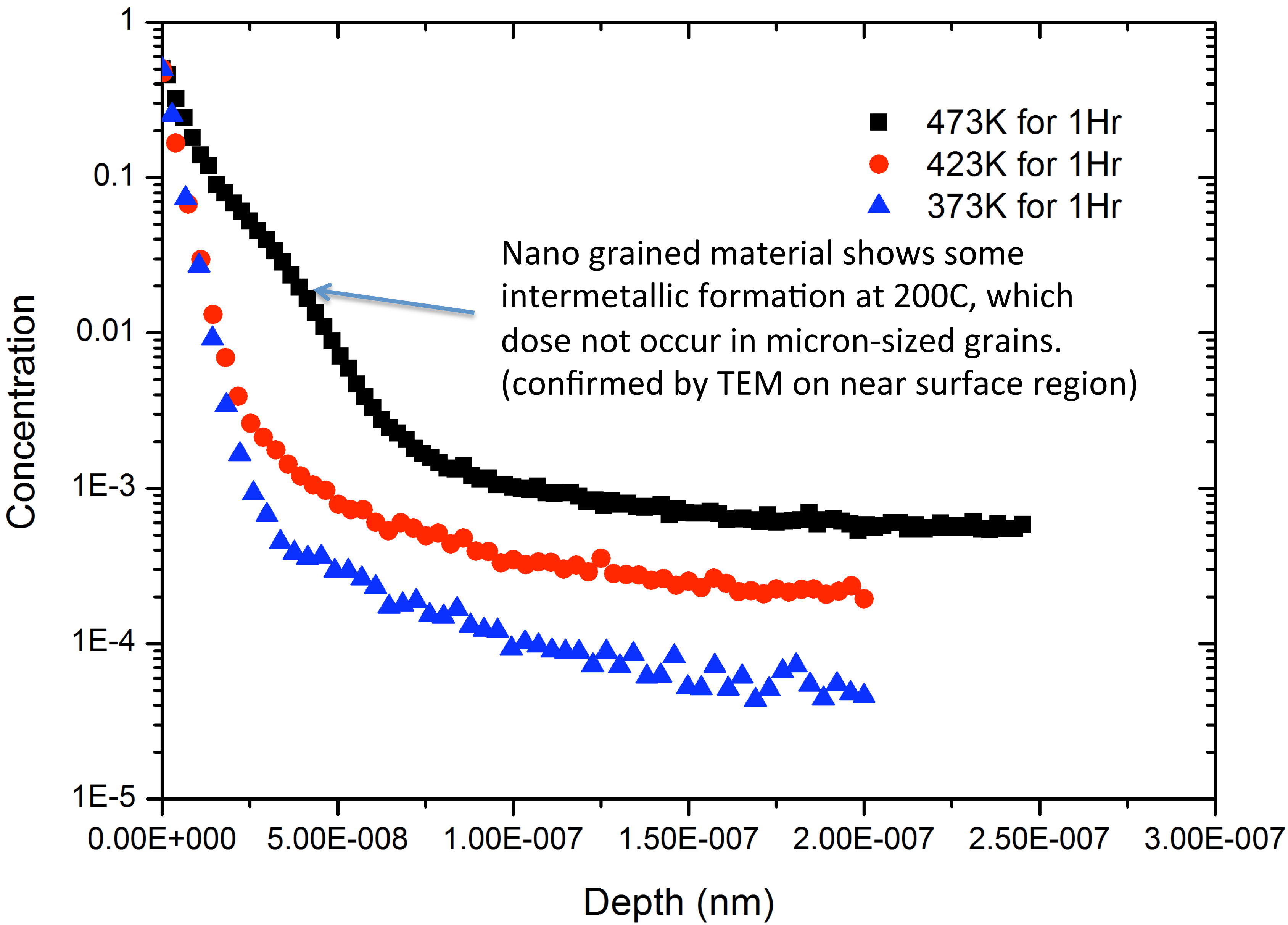




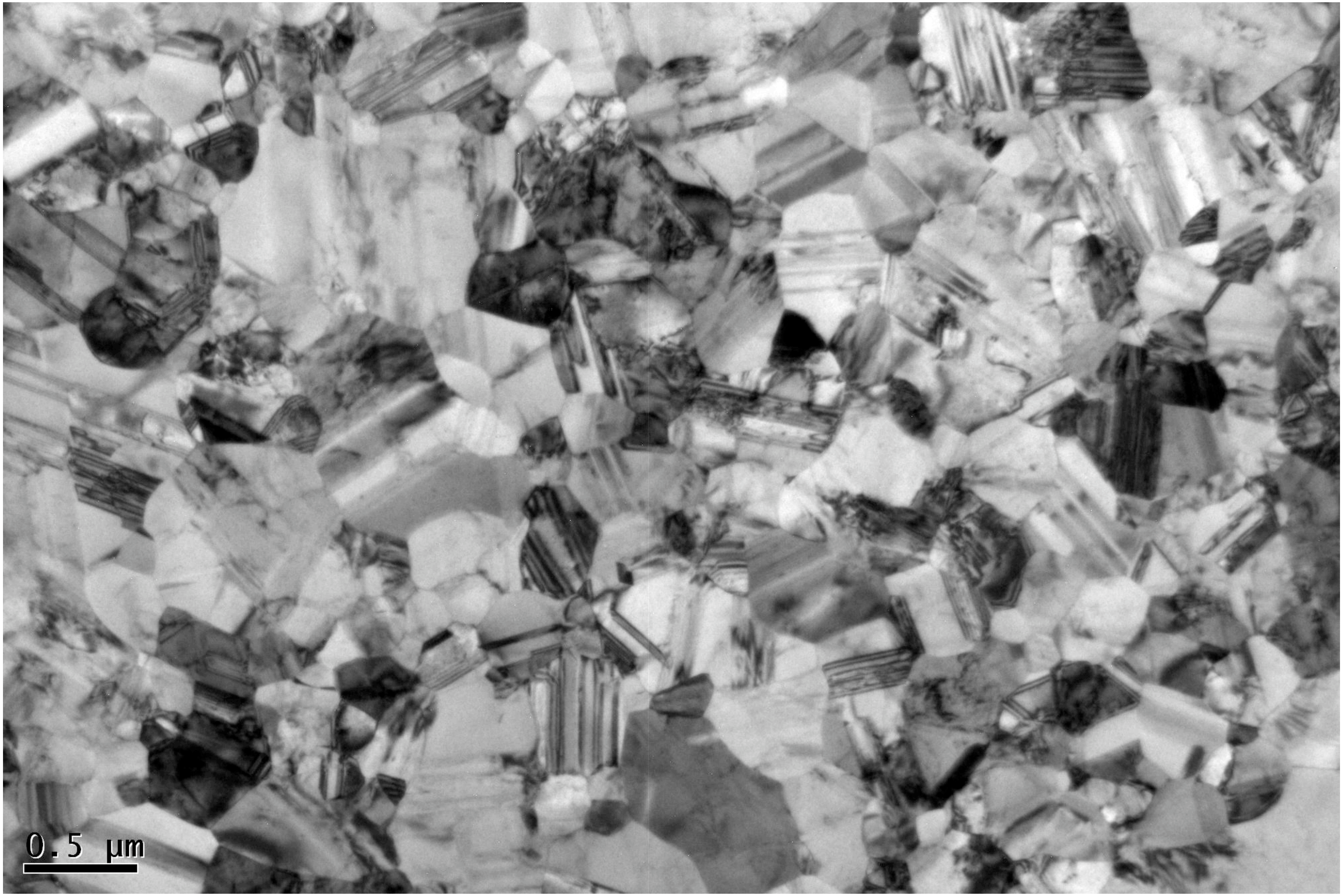
SIMS Raw Data Translated into Real Concentration by Calibration Results

Pure copper

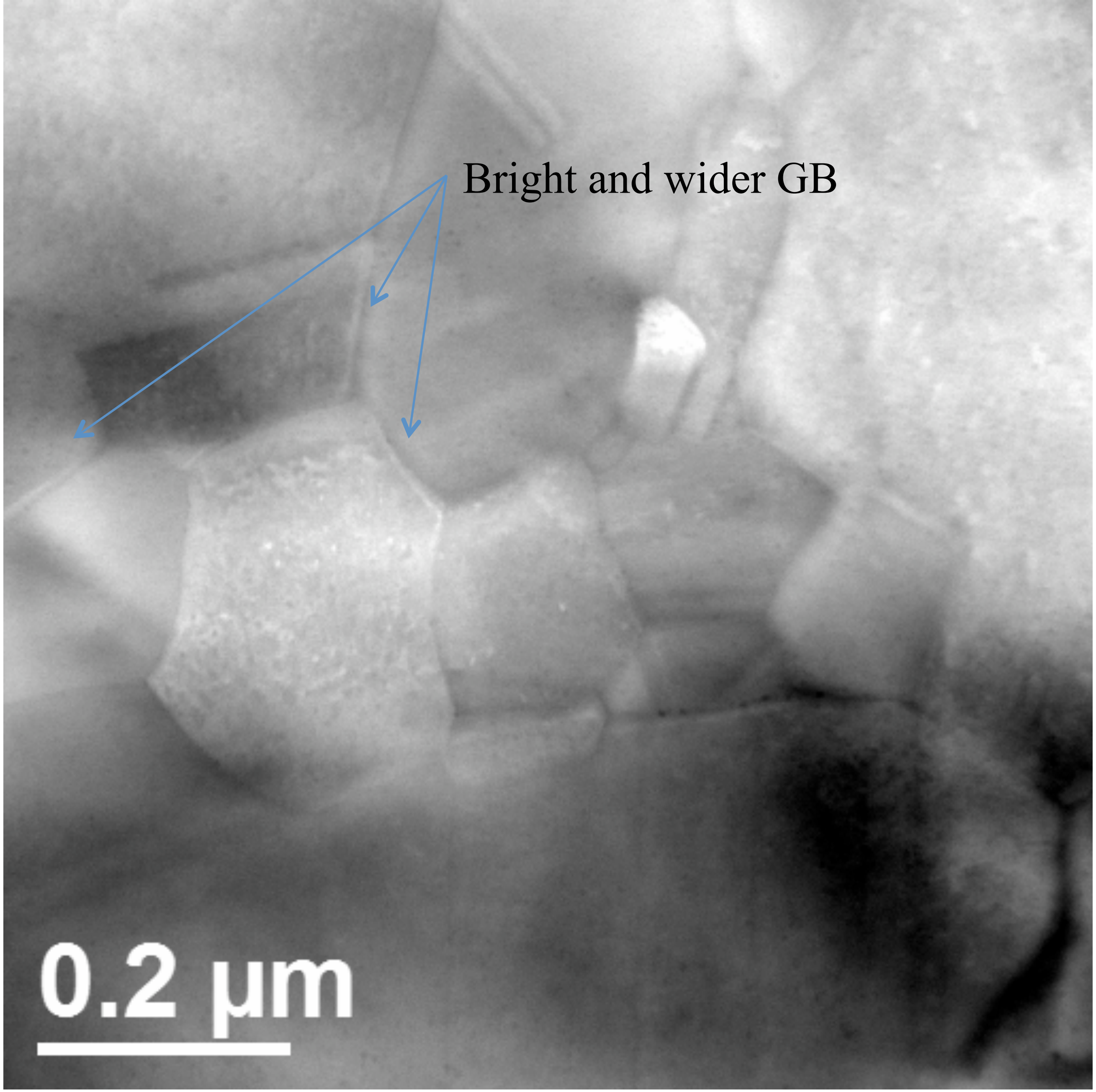
- Pure copper is the reference state to compare with the Cu-Bi system
- As-deposited nanograined samples were compared with annealed samples to look for indications of any size effects. Size effects at grain boundaries may be suggested by the AGG (GB relaxation?) that these samples typically undergo between ~200-300C.



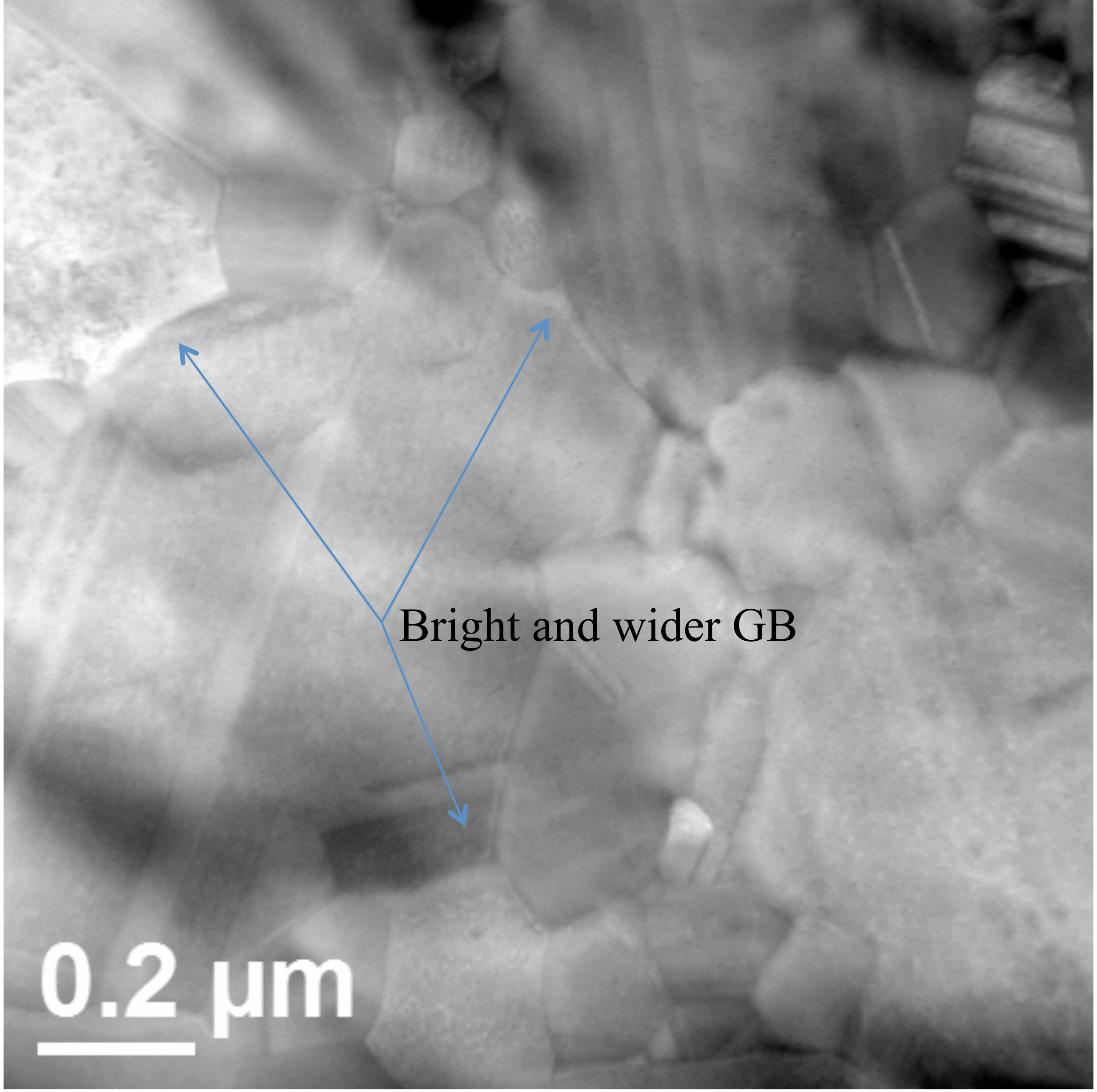
Au coating on pure Cu (as-deposited) annealed at three temperatures



Bright-field TEM image of pure Cu as-deposited (Twinning and Grain size)



Au-enriched wider GB: GB immigration evidence (Z-contrast) at 473K



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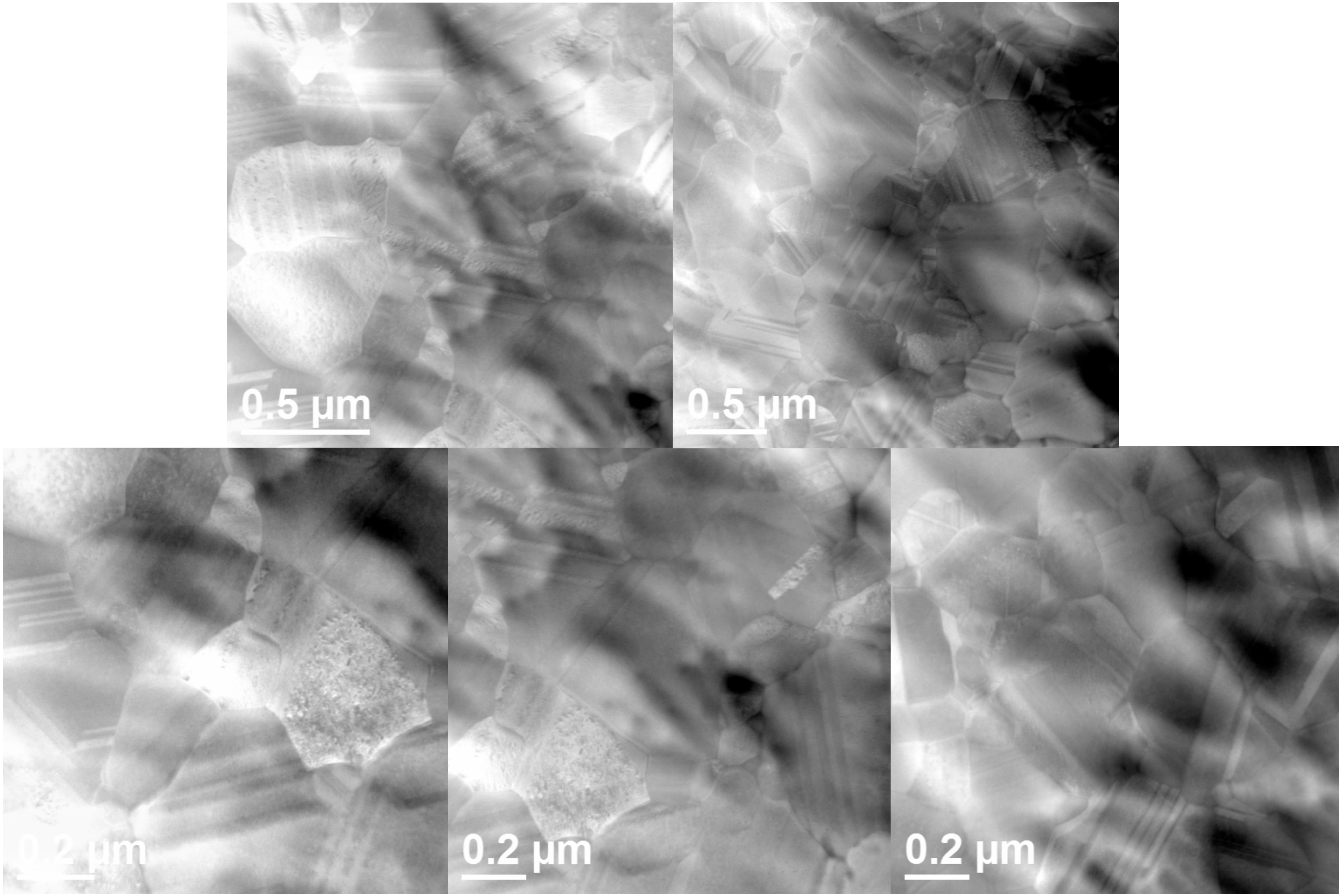
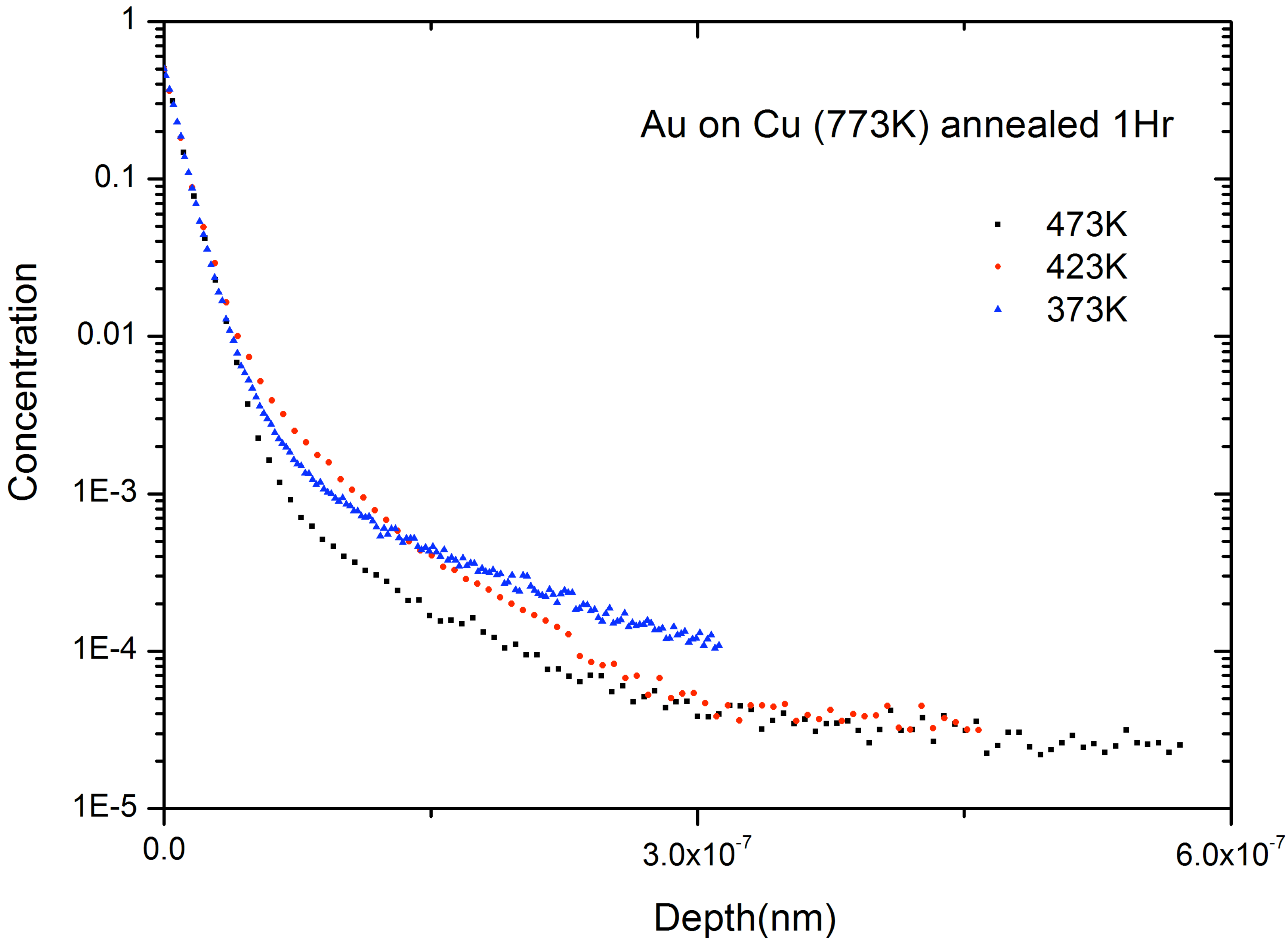
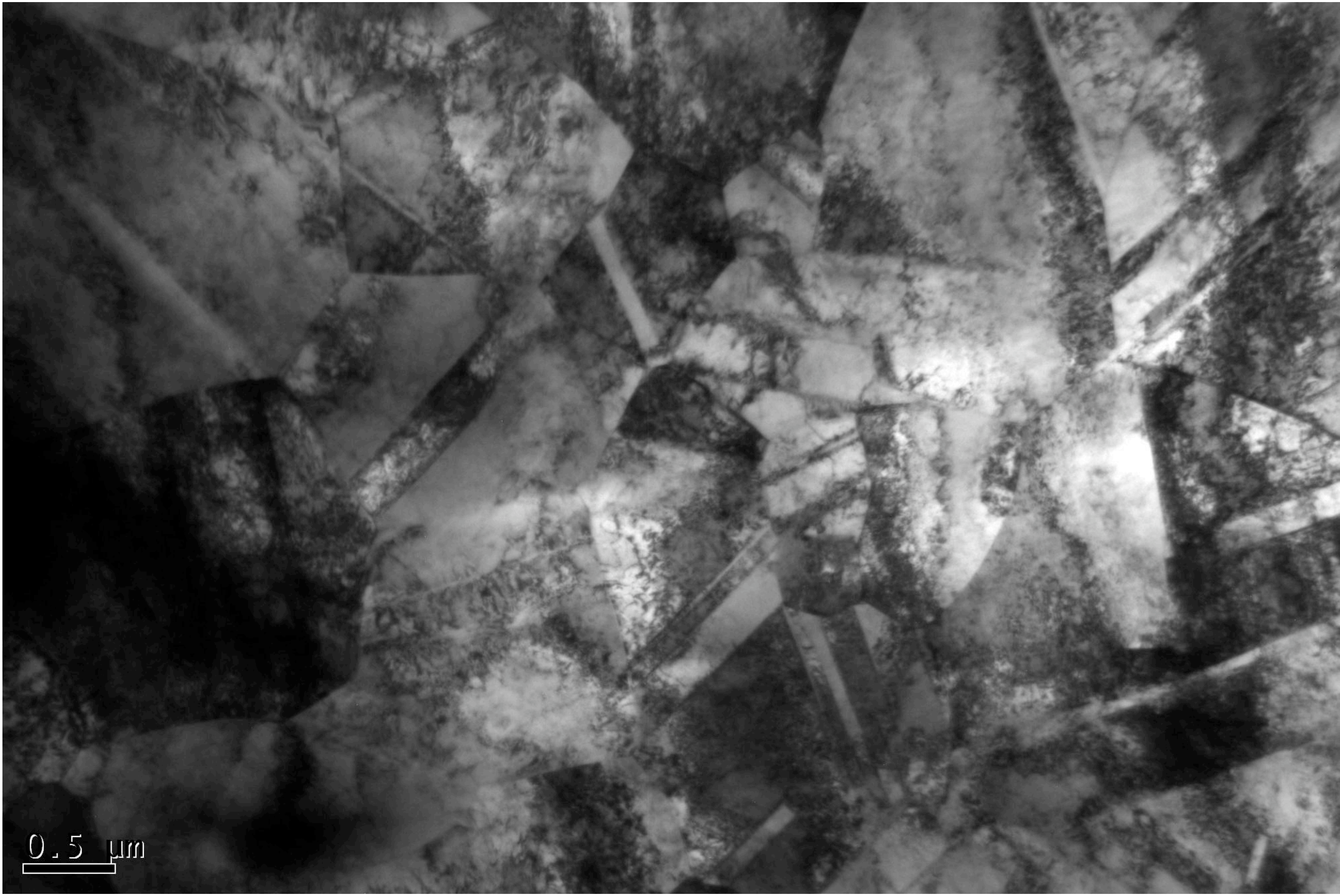


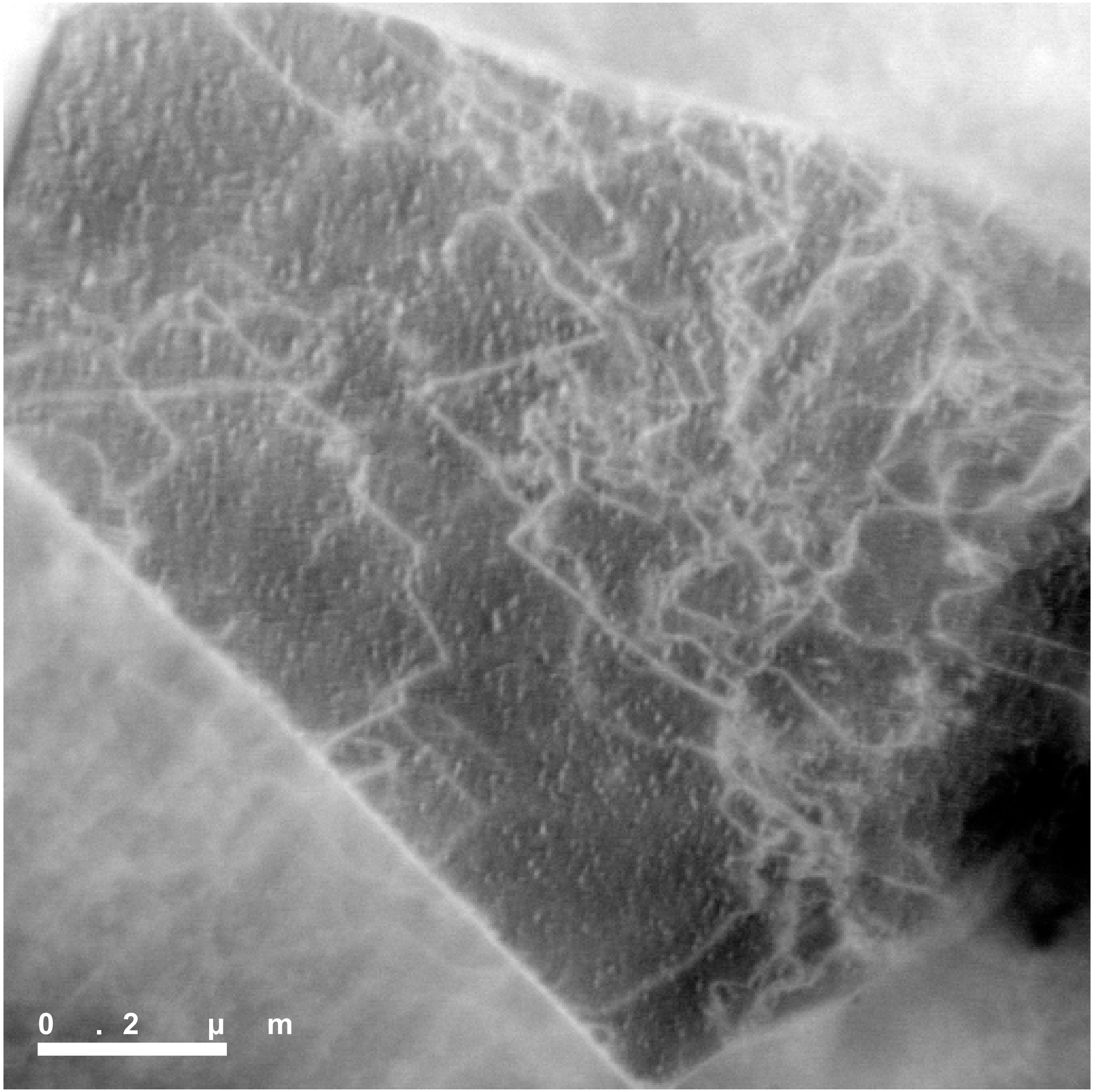
Au-enriched wider GB: GB immigration evidences at 473K



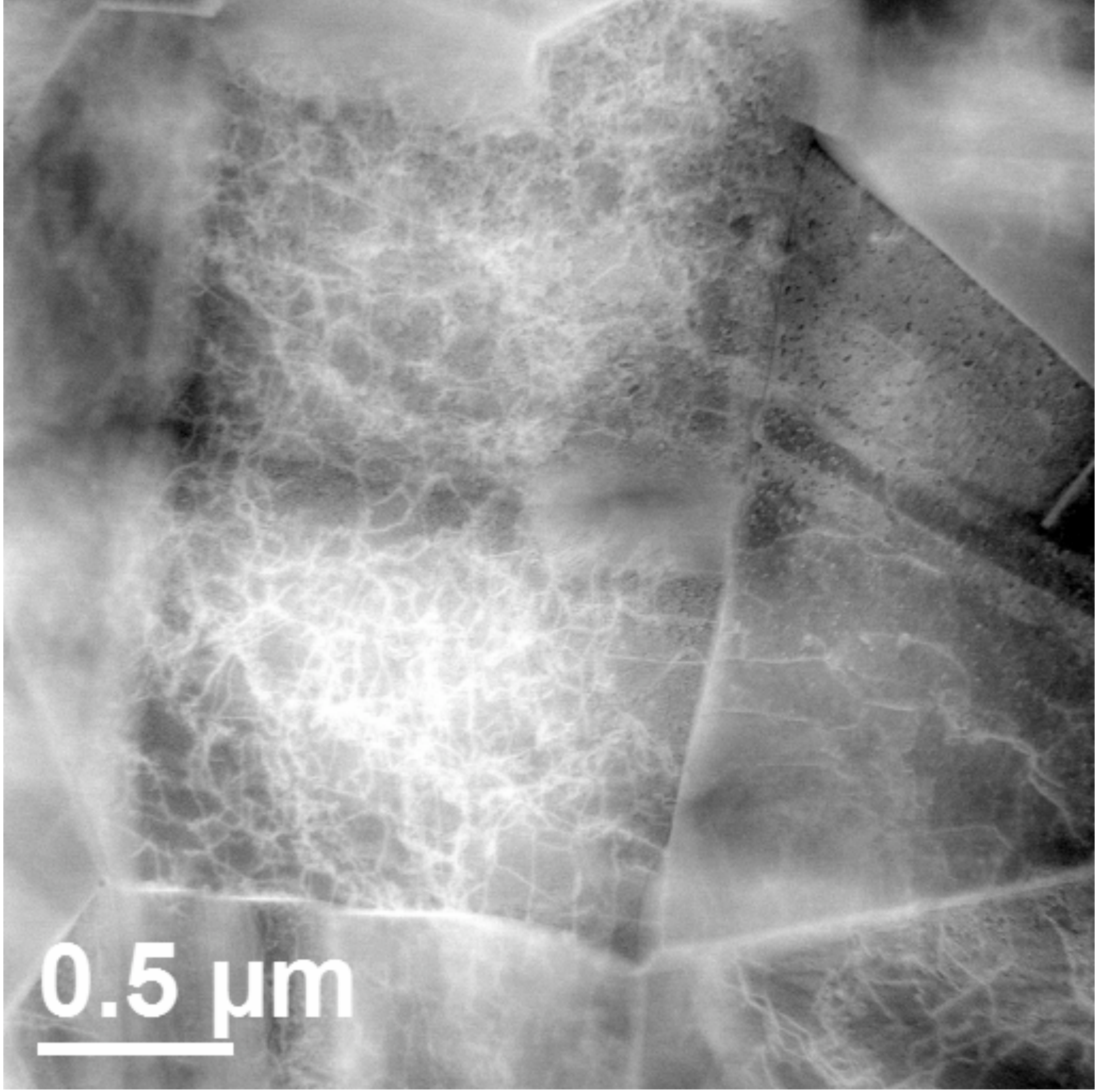
Au diffusion profile in Cu-773K pre-annealed



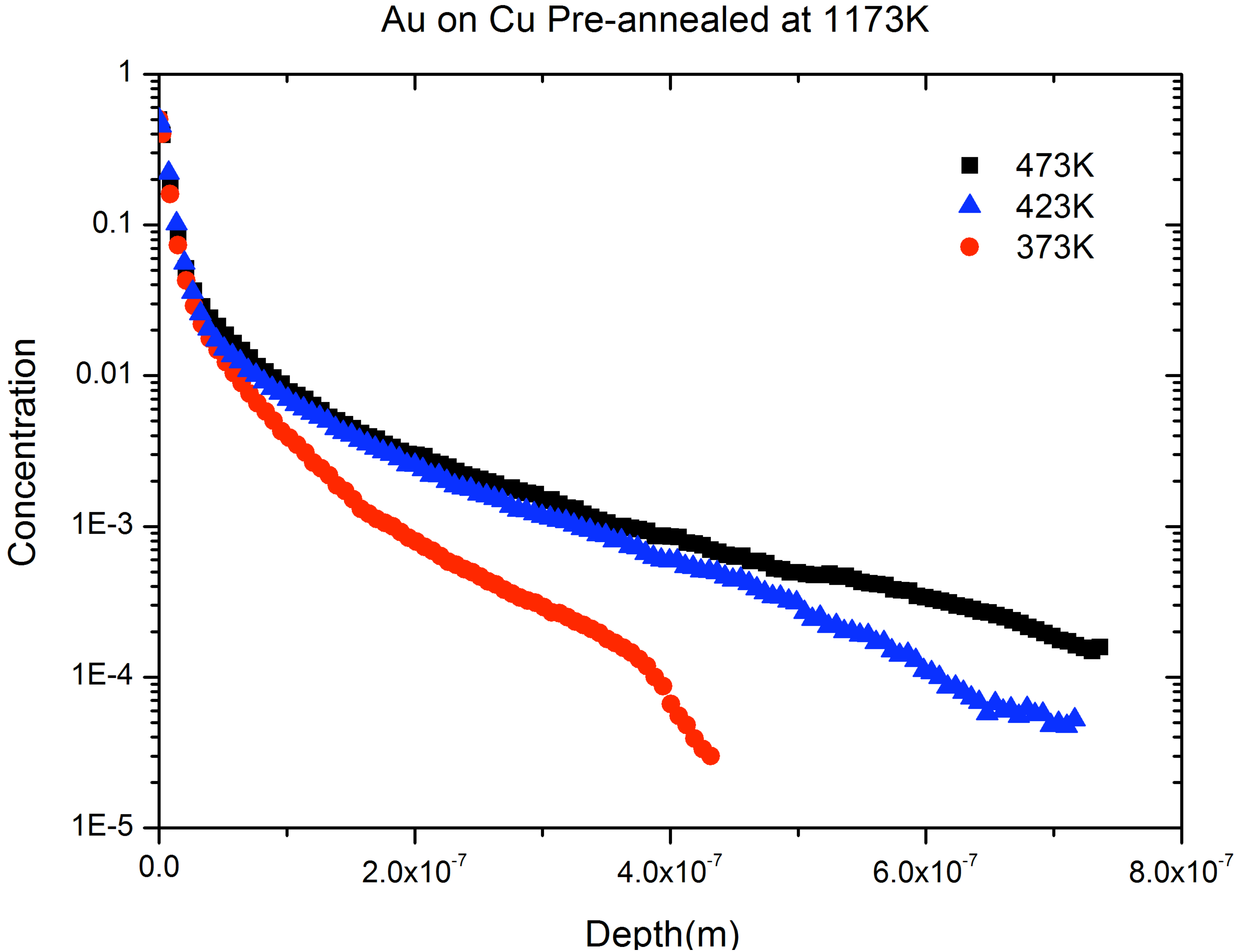
Cu-773K pre-annealed matrix (high density of dislocation-network)



Z-contrast of Au diffusion leakage to dislocation-network from GB



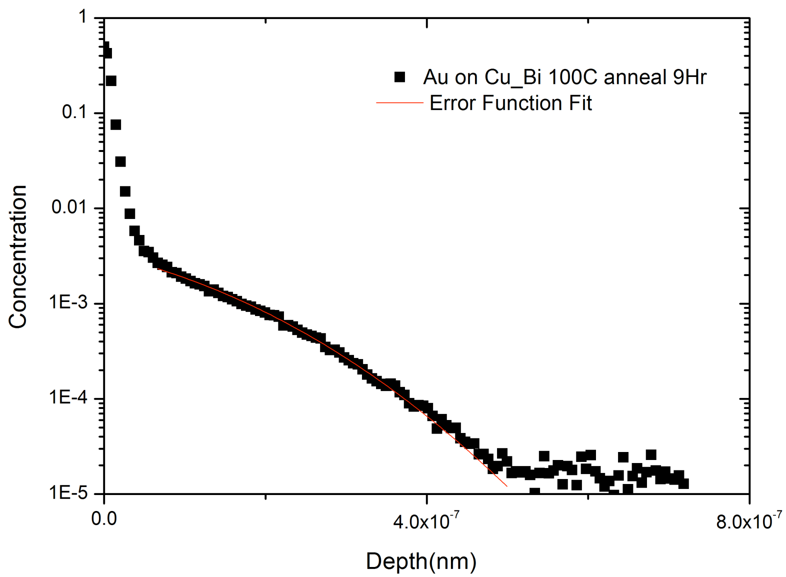
Z-contrast of Au diffusion leakage to dislocation-network from GB

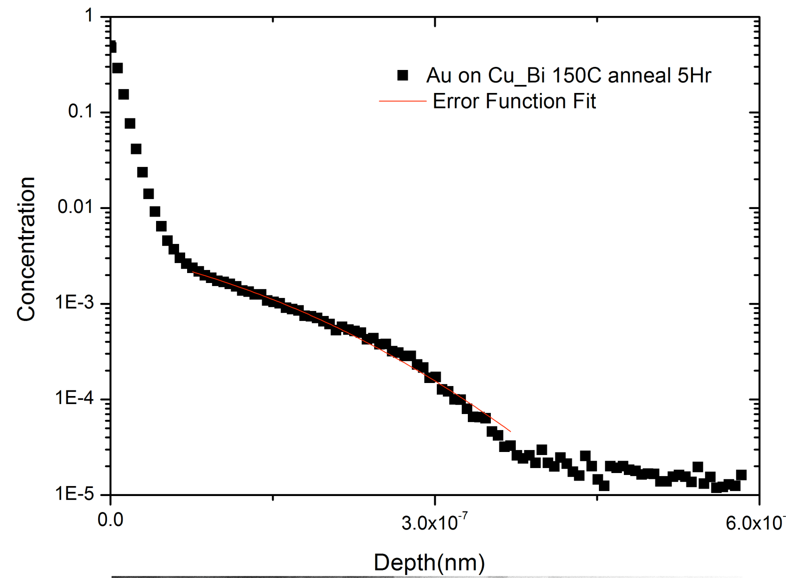

Au on Cu Pre-annealed at 1173K
473K
423K
373K
Concentration
Depth(m)
1
0.1
0.01
1E-3
1E-4
1E-5
0.0
2.0x10-7
4.0x10-7
6.0x10-7
8.0x10-7

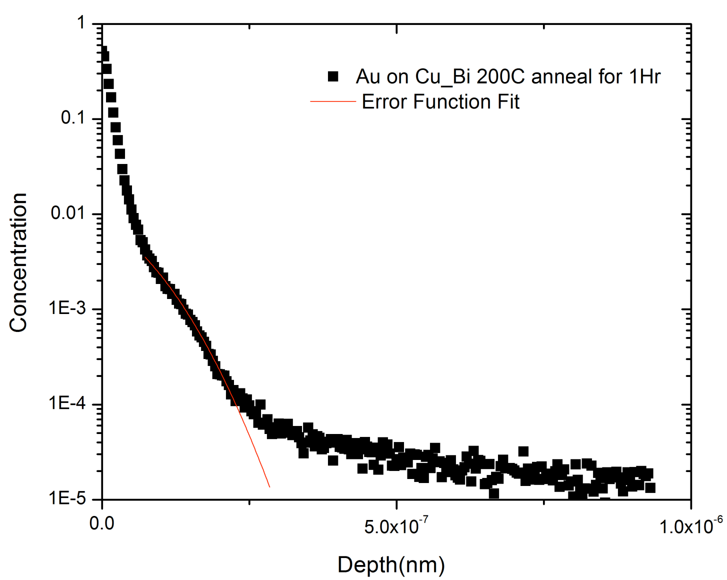
Bi-doped Cu

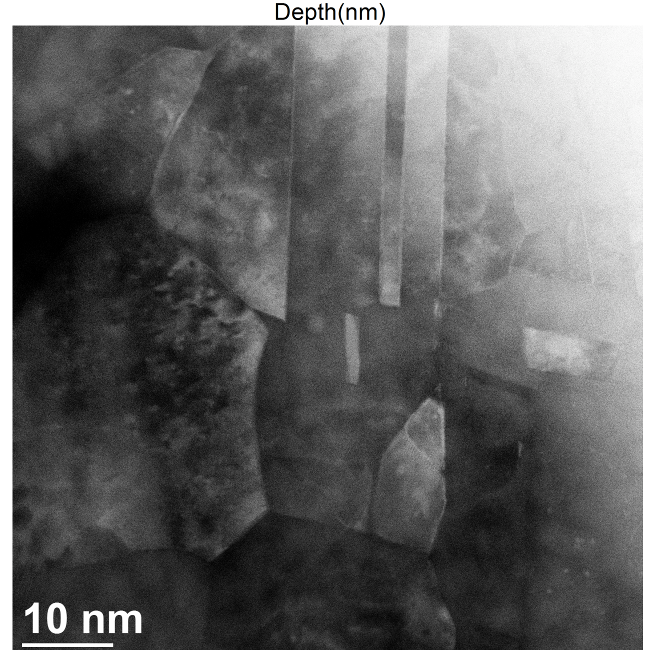
- Characterizing transport kinetics with expectation that analogous GB complexion phenomena will exist in Cu-Bi as Ni-Bi
- Samples pre-annealed near, not in contact with, Bi source at 500C and 900C

773K Pre-annealed with Bi

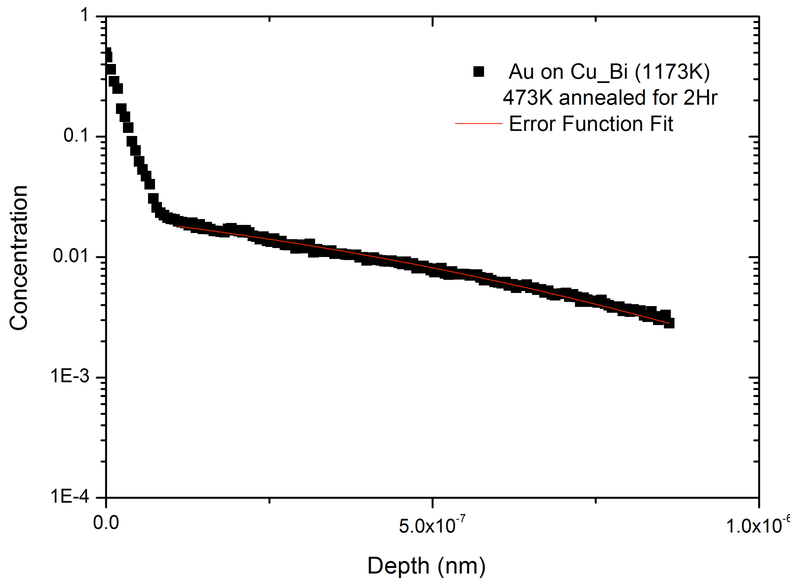


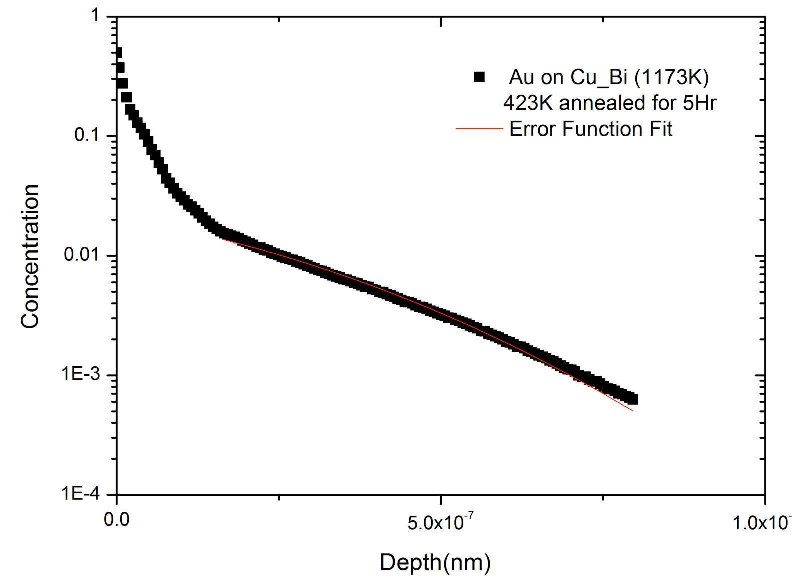


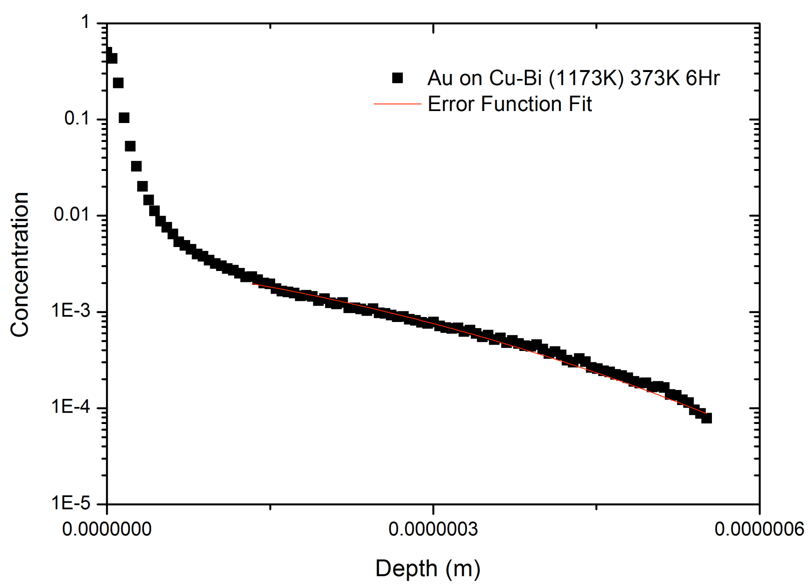


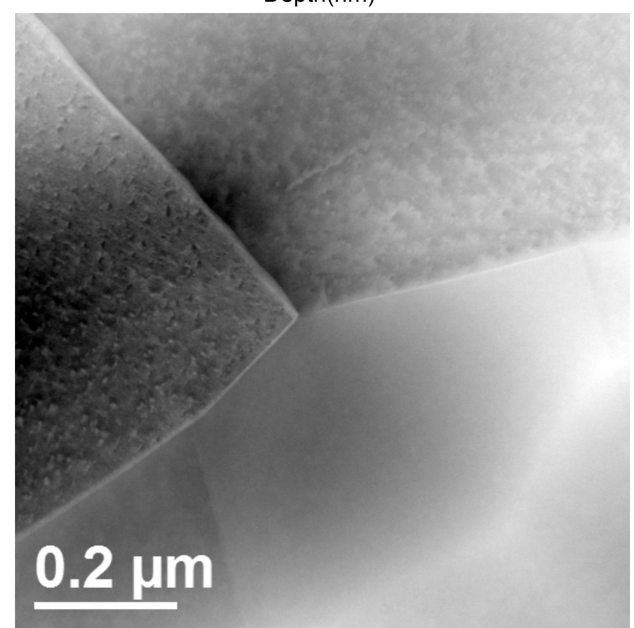


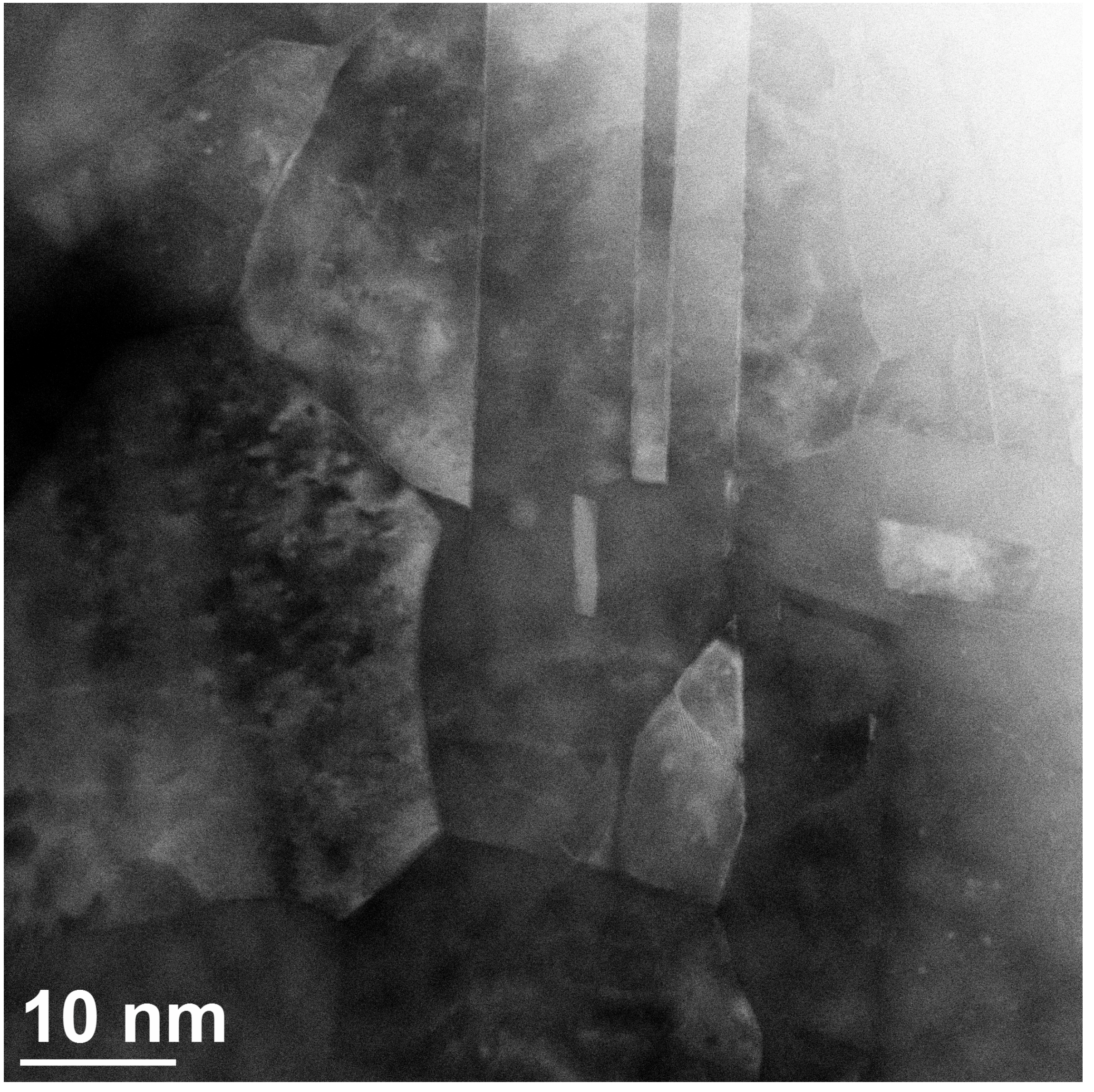
1173 Pre-annealed with Bi



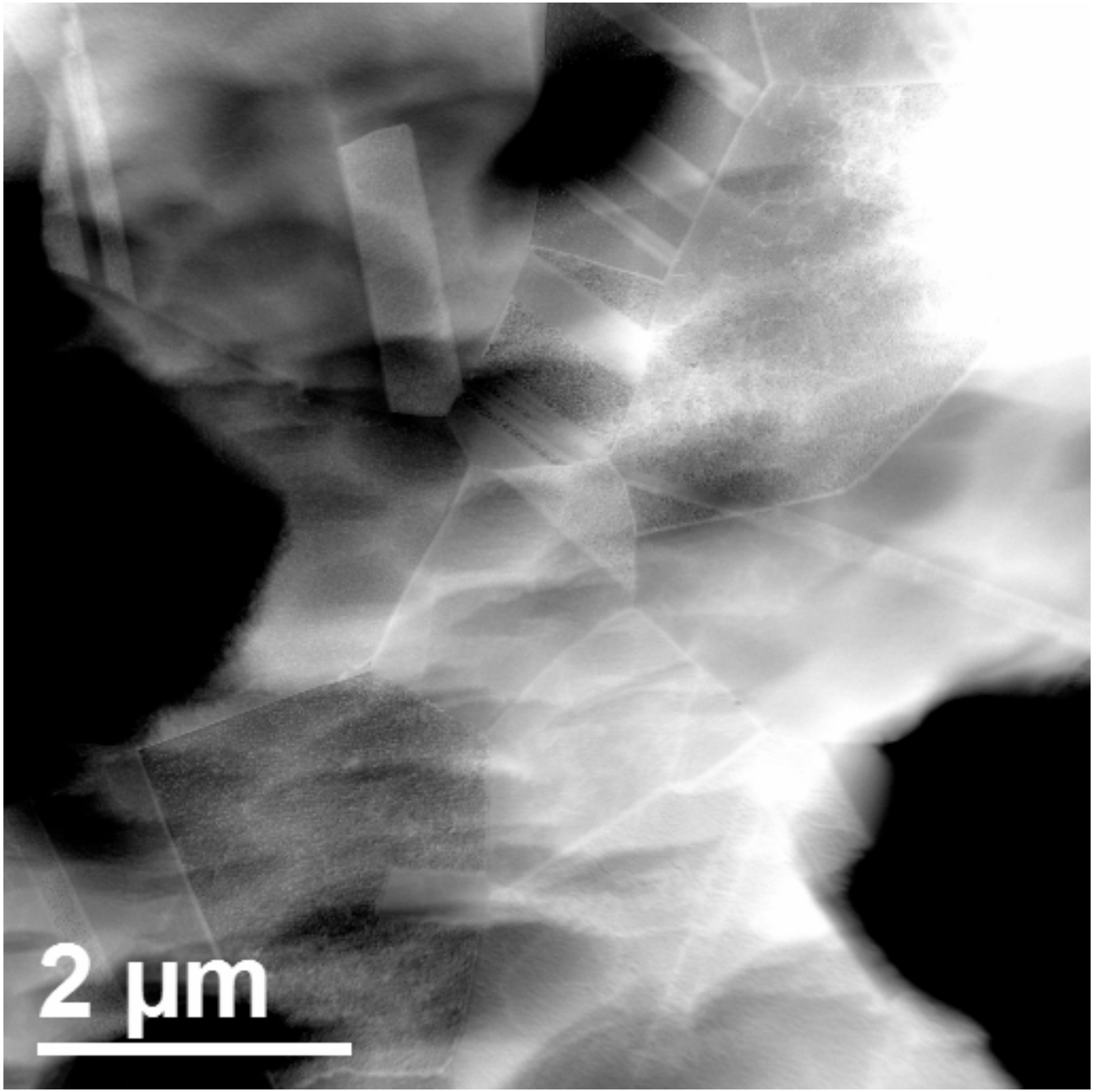




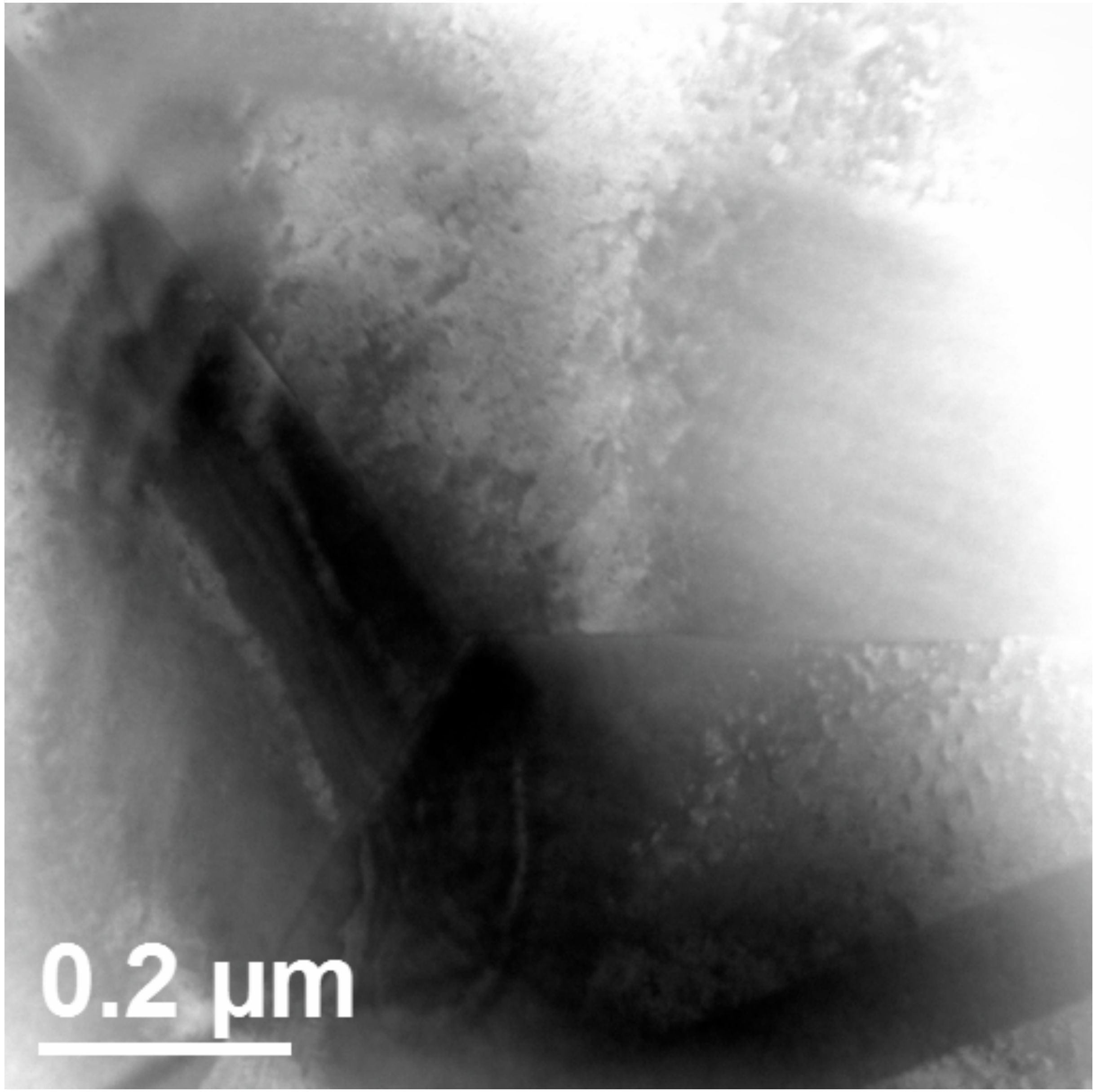




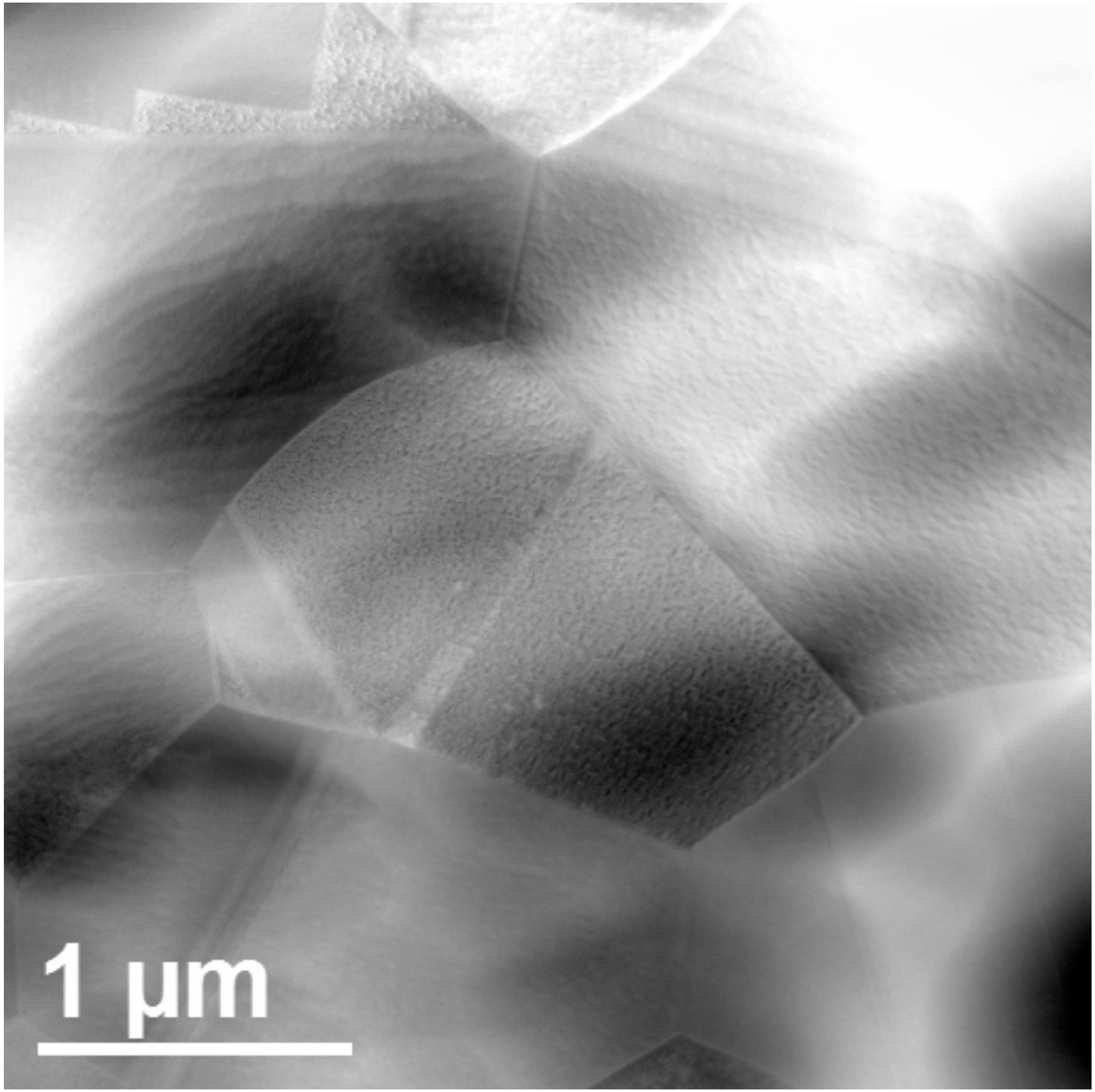
Bi diffusion along pure Cu GB Z-contrast (bright GB: Bi-enriched)



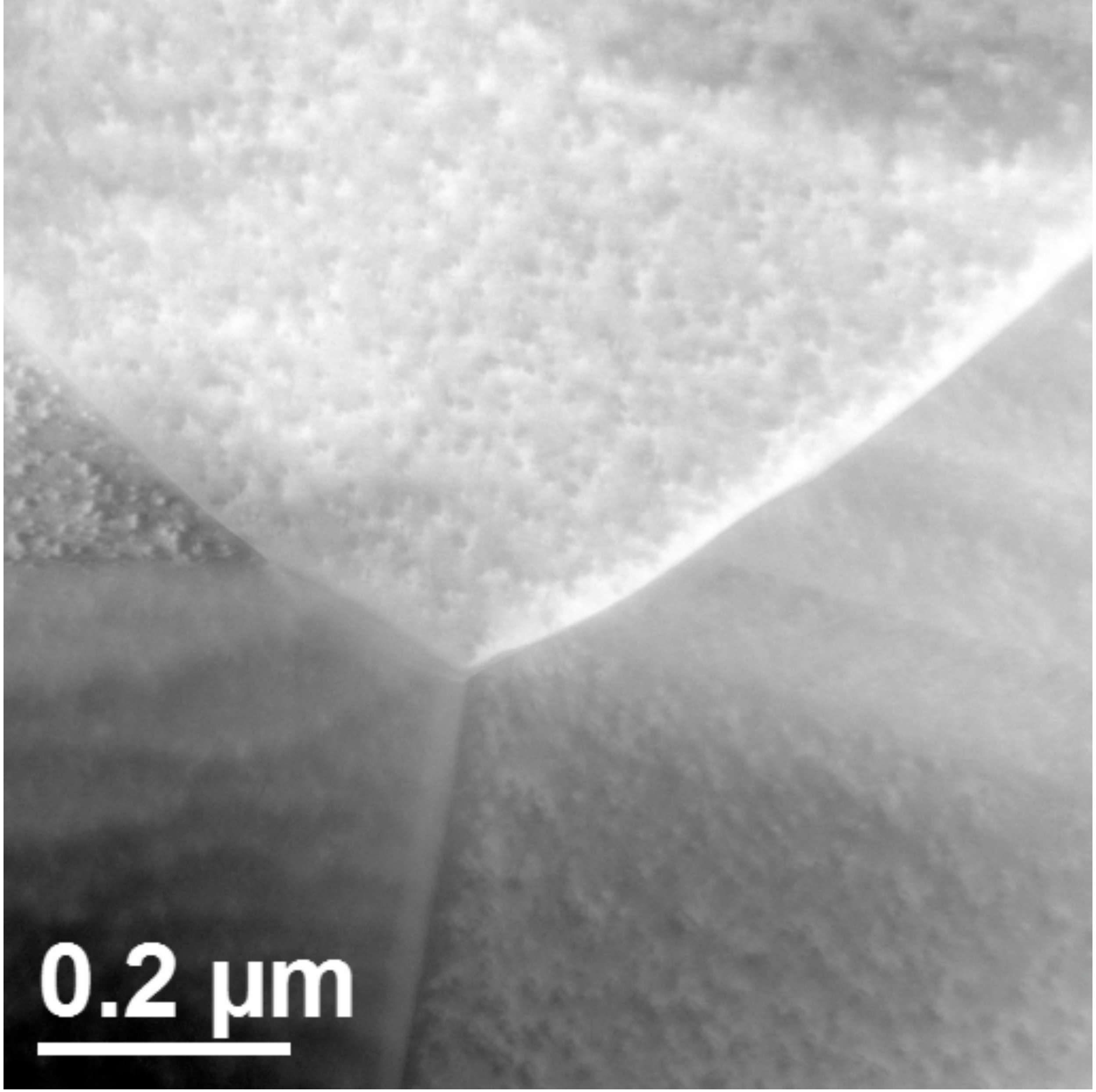
Cu-Bi annealed at 900˚C for 1hr (Z-contrast)



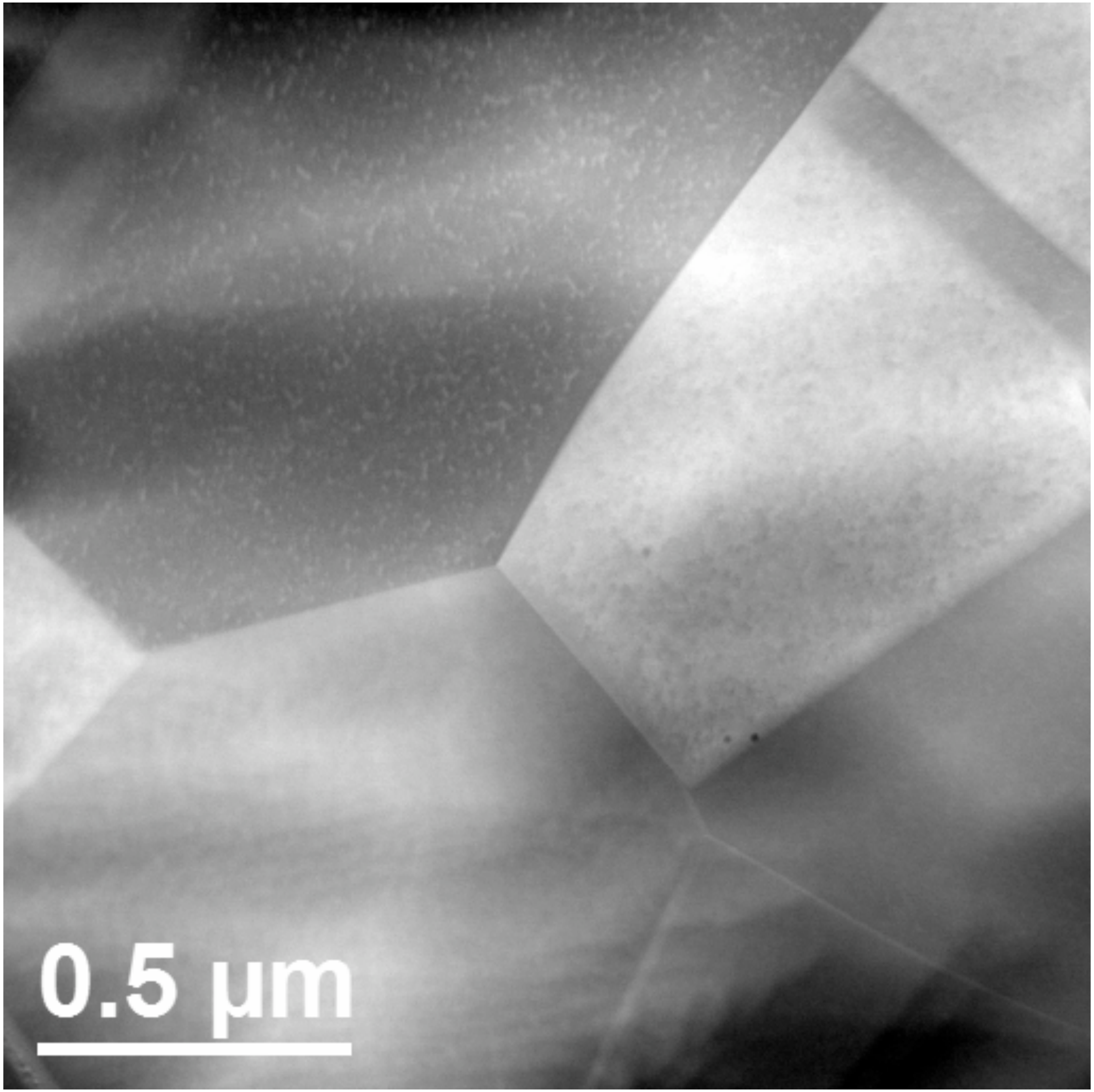
No bright contrast shown at these three GBs and triple joint point



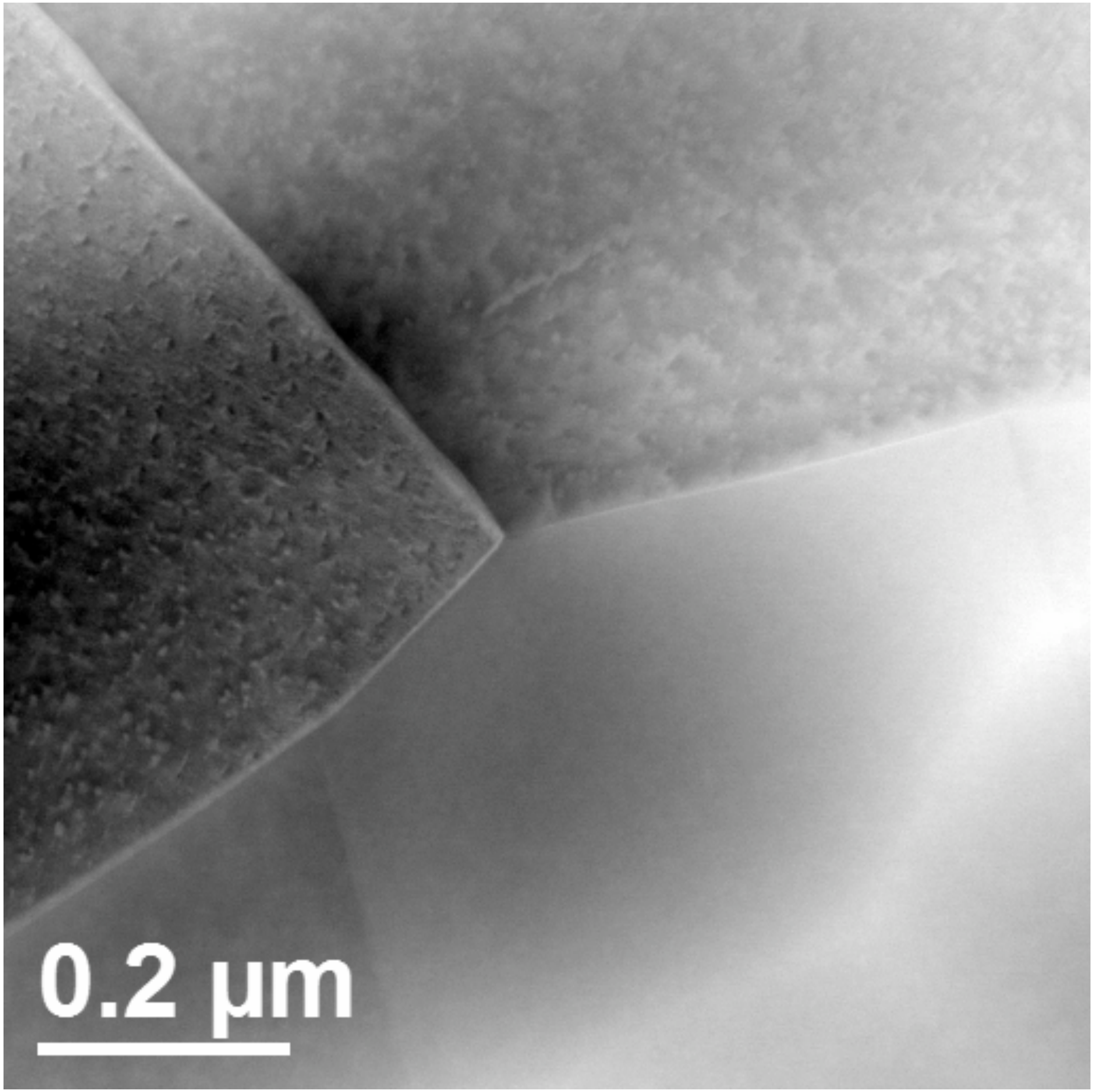
Bright contrast shown at some GBs



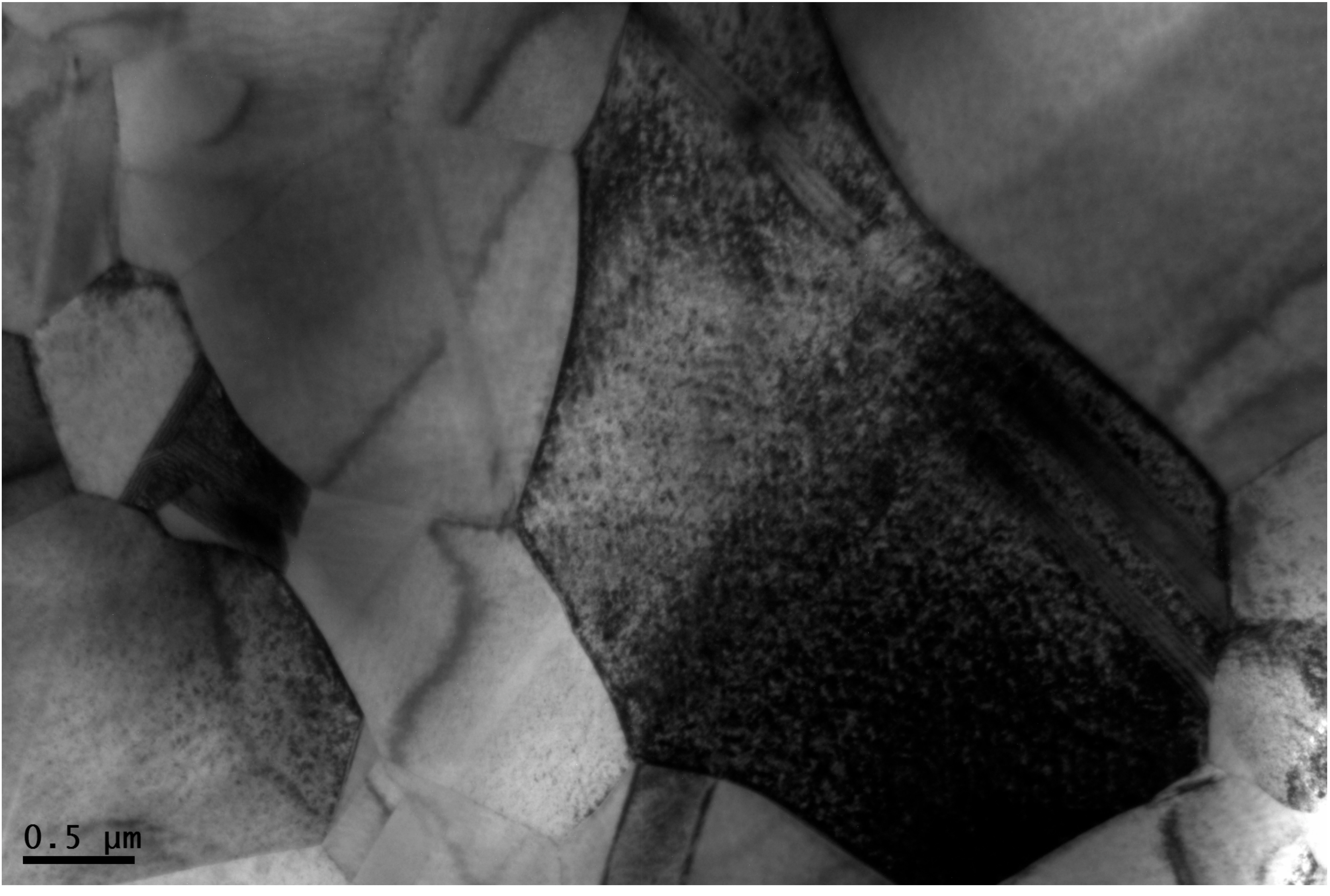
Bright contrast shown at some GBs



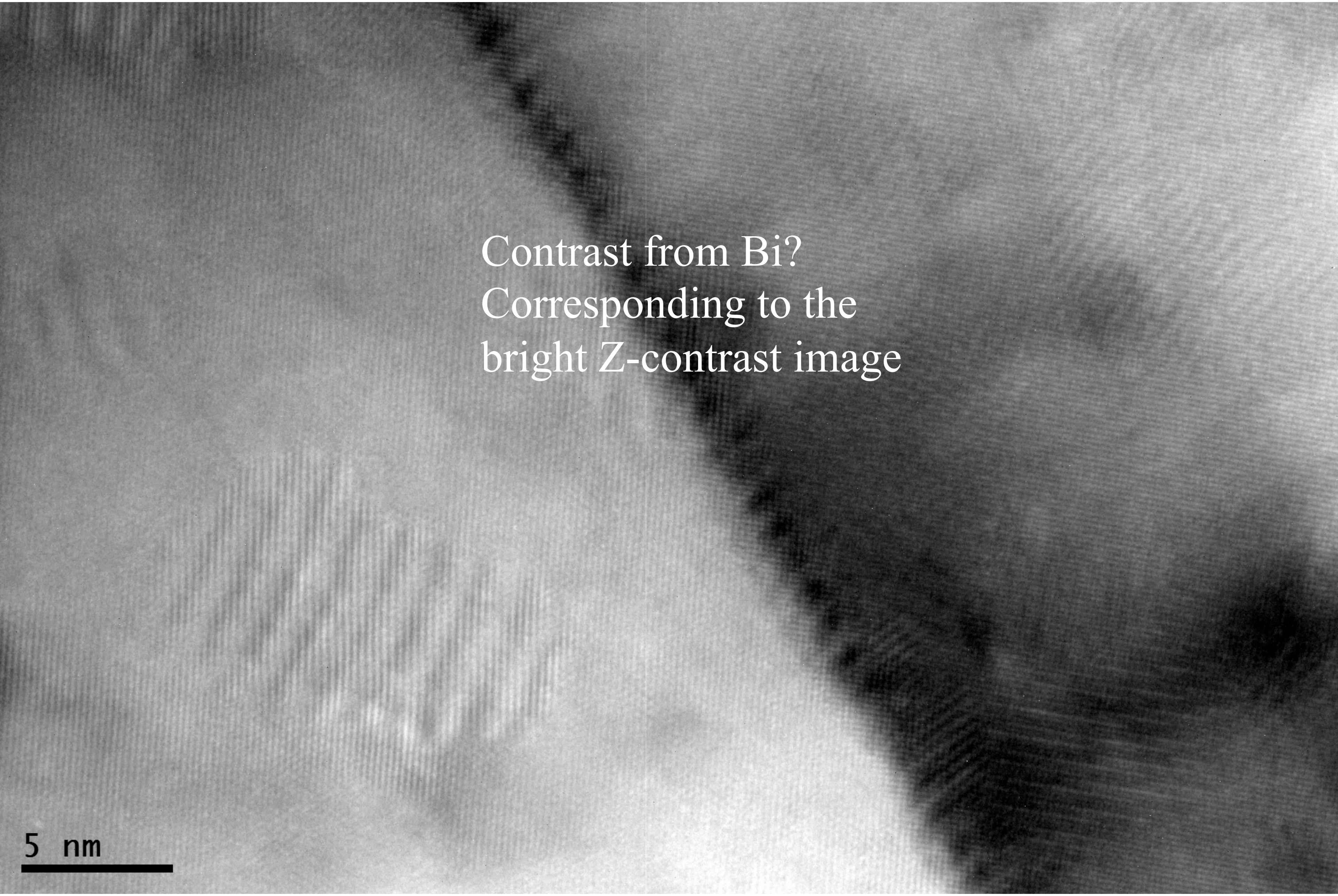
Bright contrast shown at some GBs



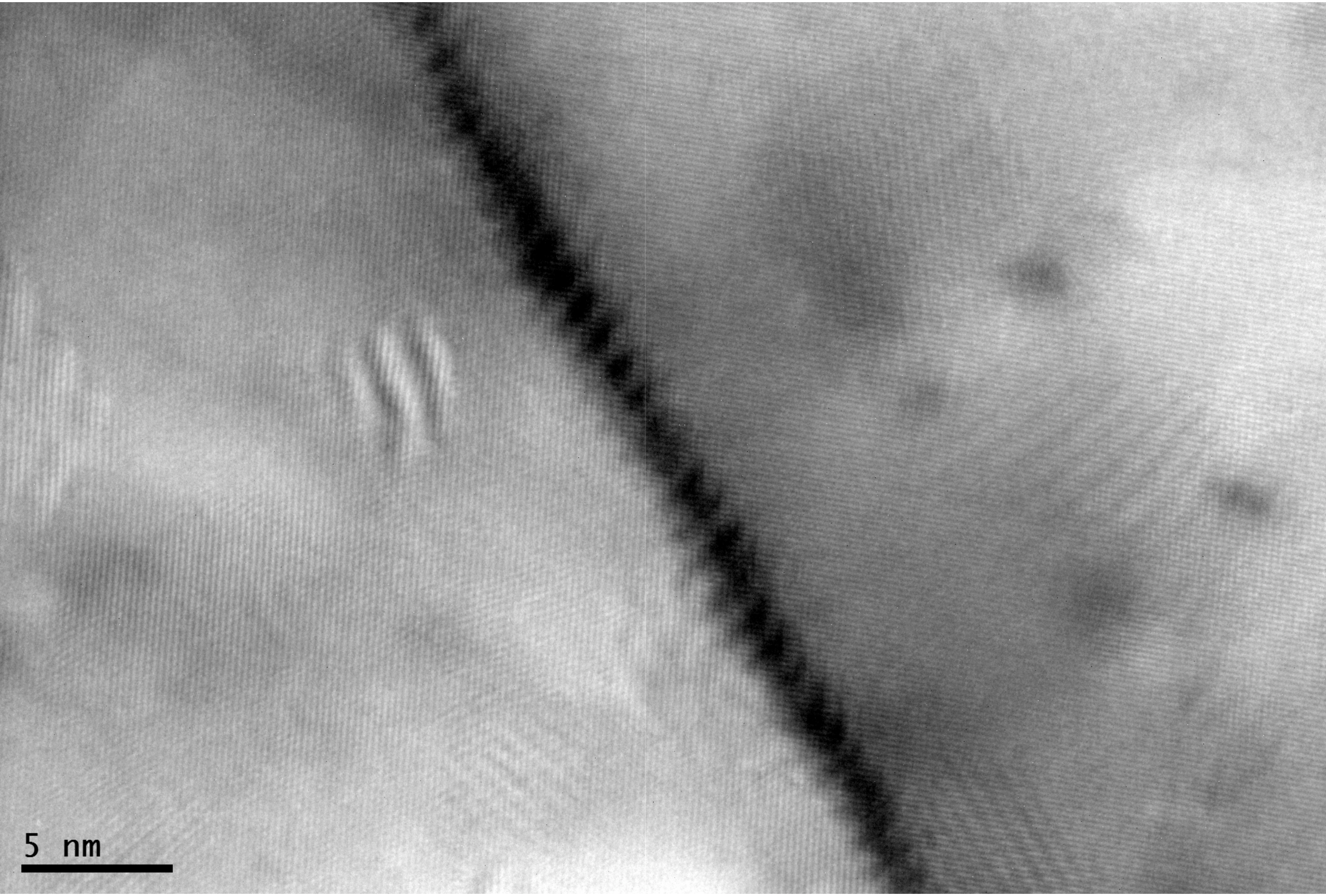
Bright contrast shown at some GBs



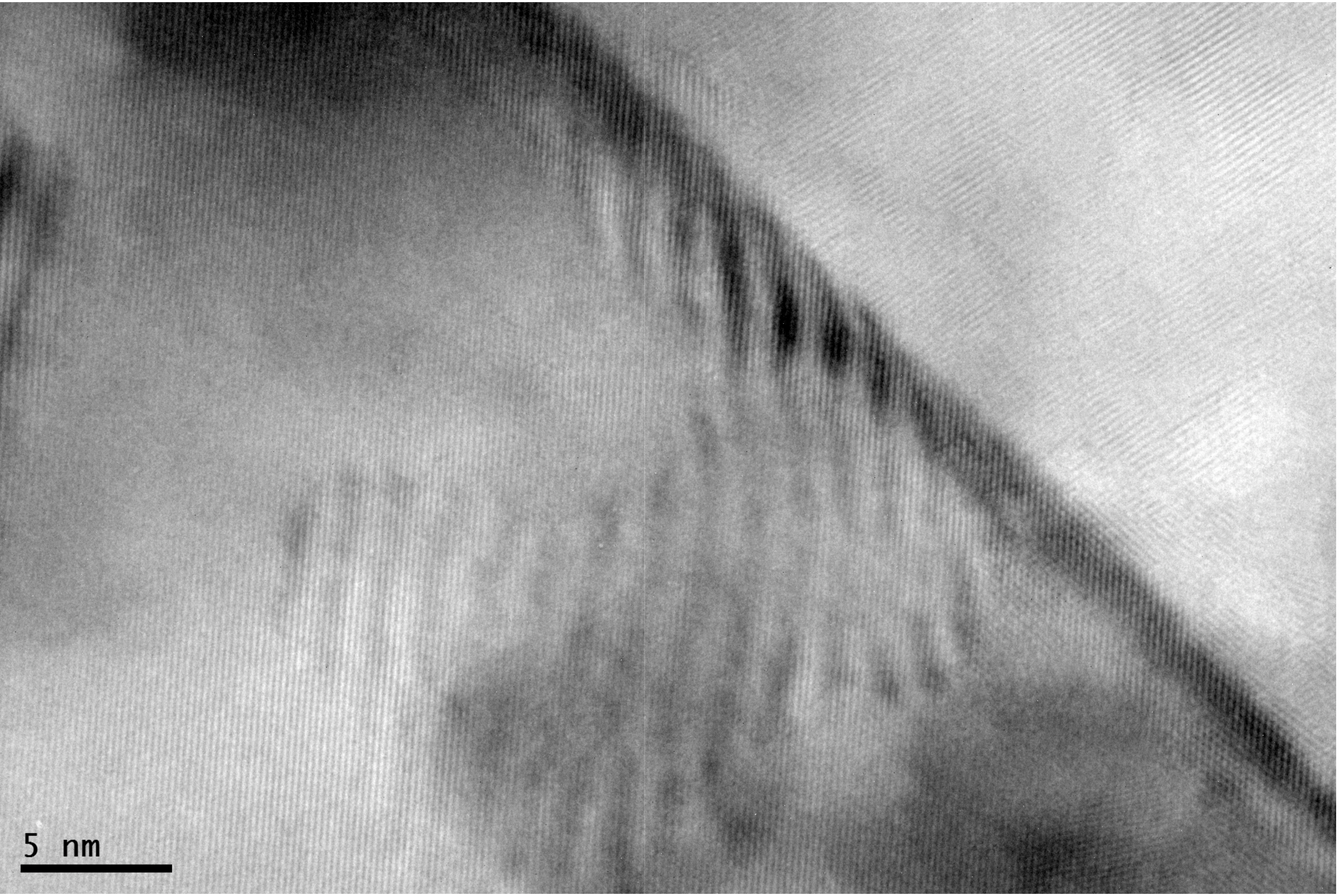
Low dislocation density in the 1173K pre-annealed Cu

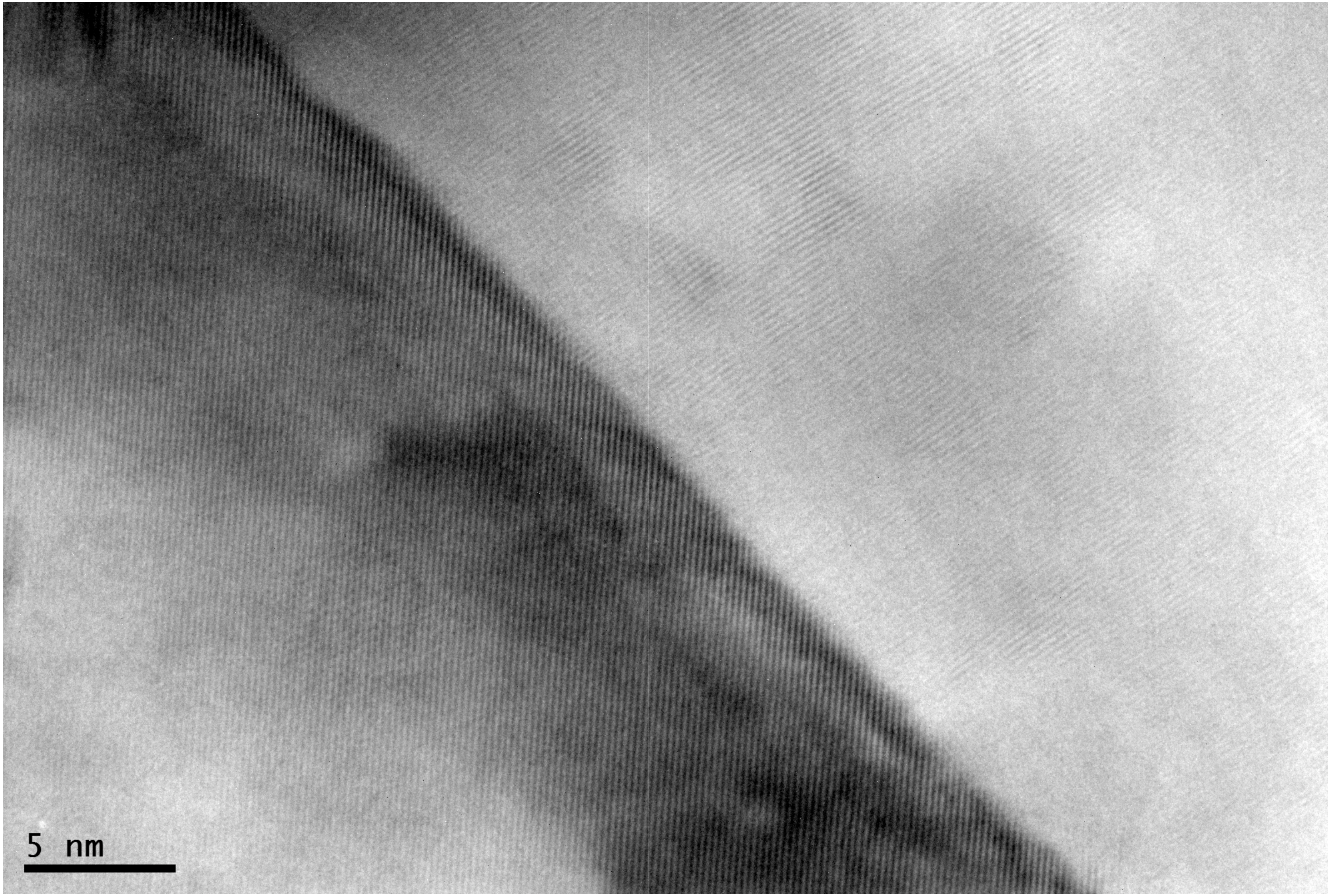


Cu-Bi 1173K pre-annealed GB image

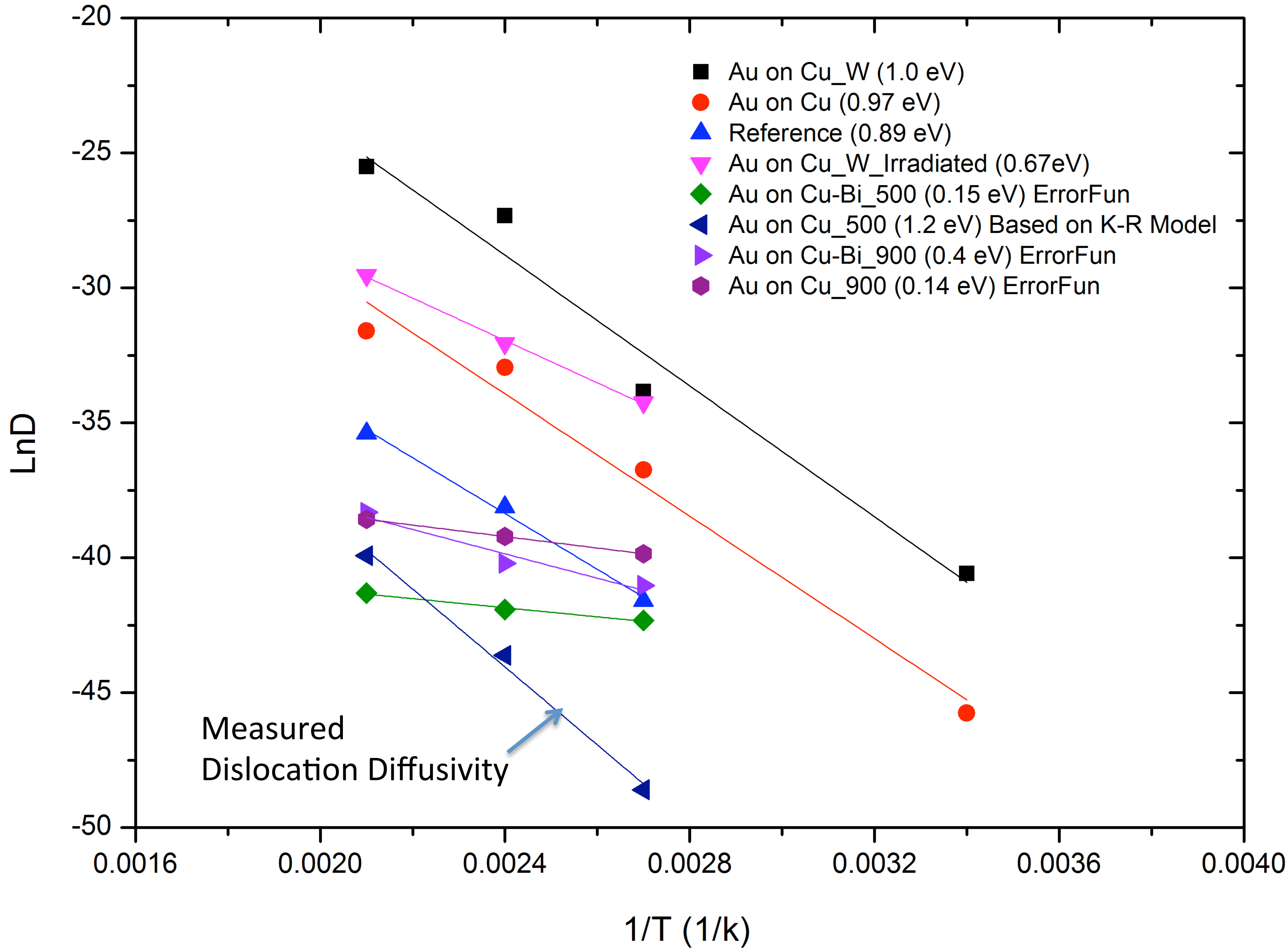


Cu-Bi 1173K pre-annealed GB image


5 nm



Cu-Bi 1173K pre-annealed GB image



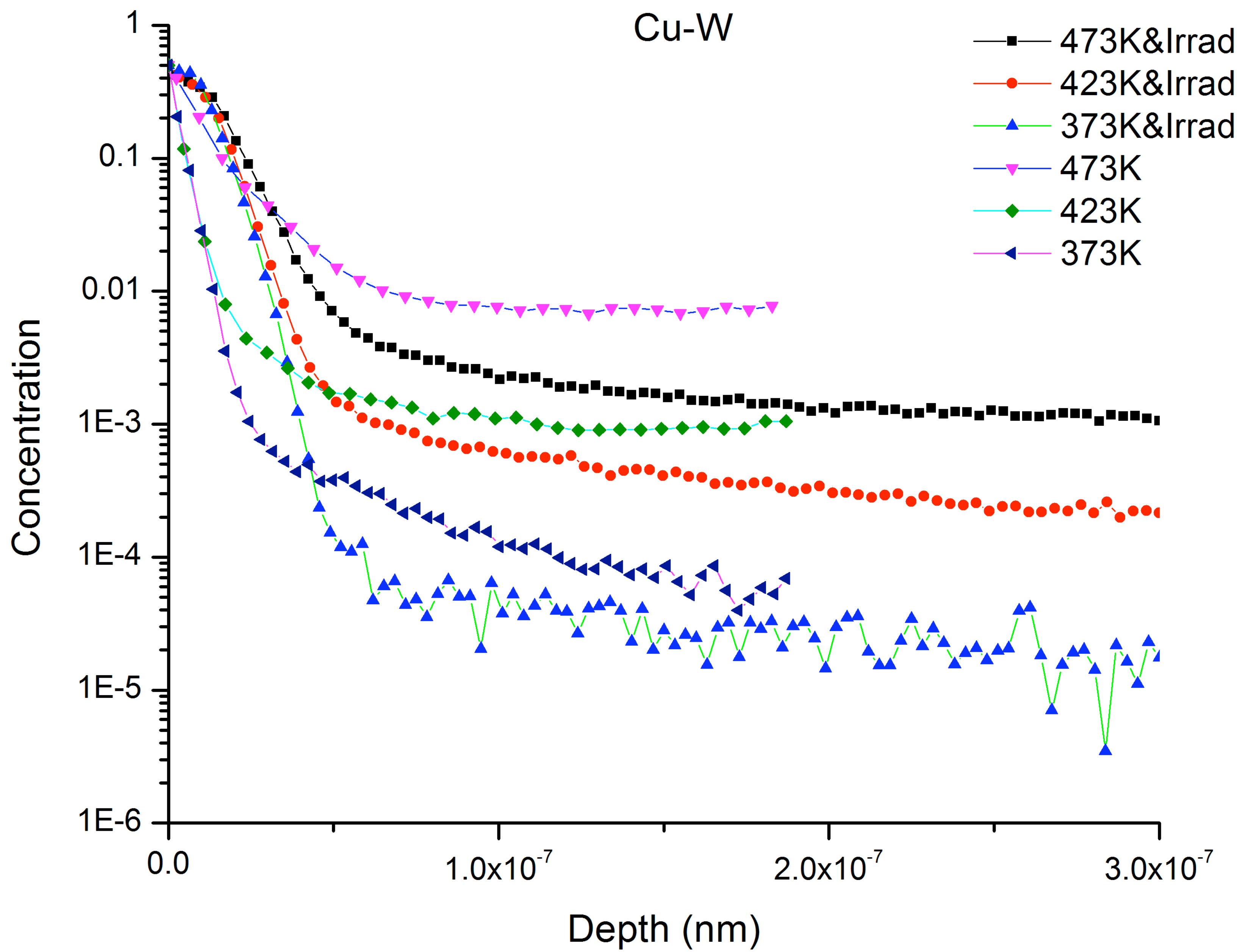
Au diffusivity-temperature dependence in the Cu(Bi) alloys

Notes about plot on previous slide

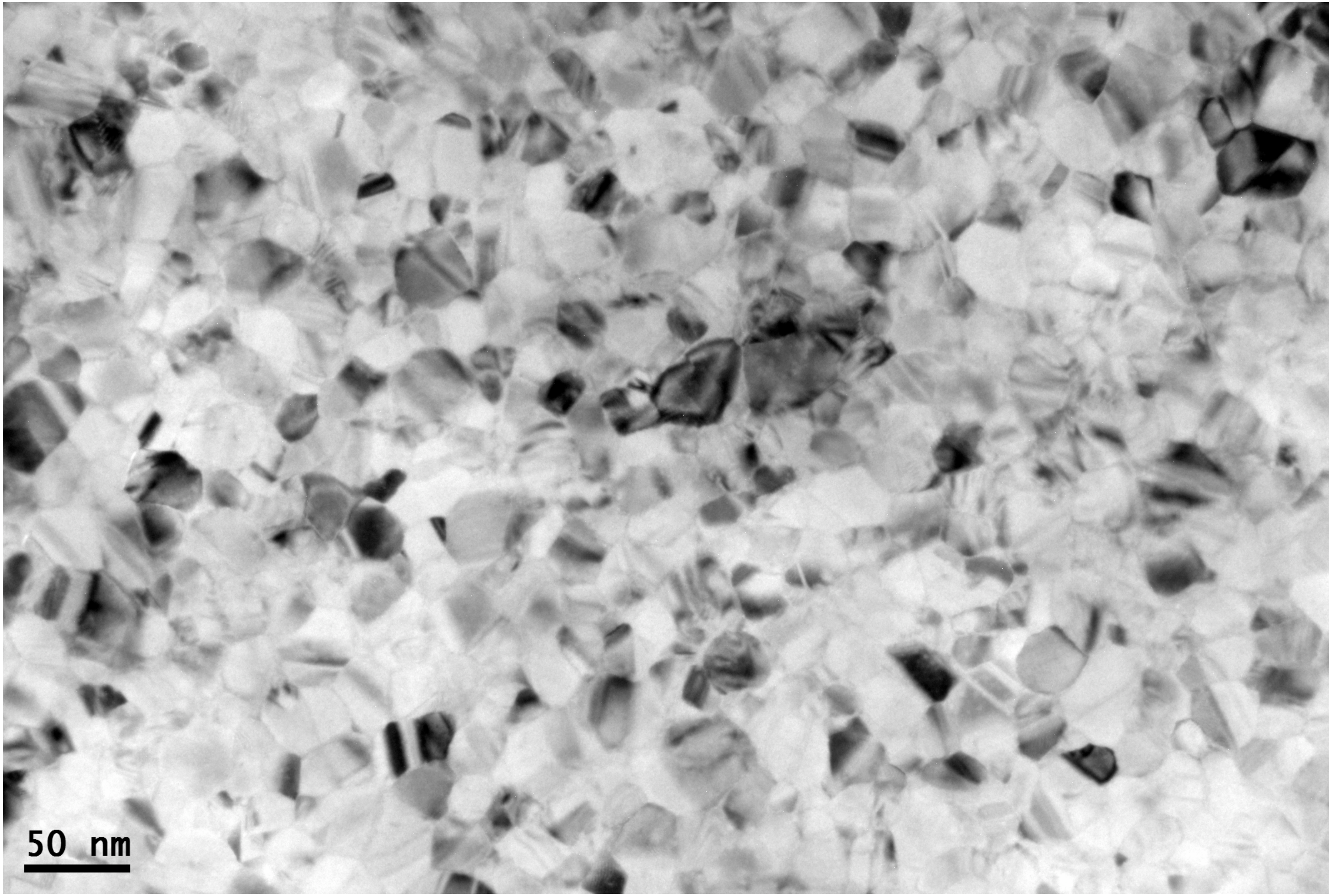
- As deposited Cu films need to be scaled to grain growth rate not lattice diffusivity from the Leclaire function. This is being measured now
- The grain boundary diffusivity of the dislocation free pure Cu data for the sample pre-annealed at 900C is taken to be representative of the GB diffusivity of the sample pre-annealed at 500C. From this the dislocation diffusivity is extracted, which agrees reasonably with the literature (at High temp)
- The nanograined material with tungsten is also not scaled appropriately, yet because an appropriate effective diffusivity of the near surface 'matrix' must be calculated appropriately. Currently the lattice diffusivity is used, but is not correct.
- The data for the bismuth doped samples and Cu pre-annealed at 900C are fit with the error function and there is no concern about any multiplication factor that affects the value of diffusivity (other than the segregation constant and boundary width).
- We are currently working on making sure that all of the data are fit in a manner that is consistent with the observed microstructures before and after annealing (which has generally not been done in much of the literature).

W-doped Cu

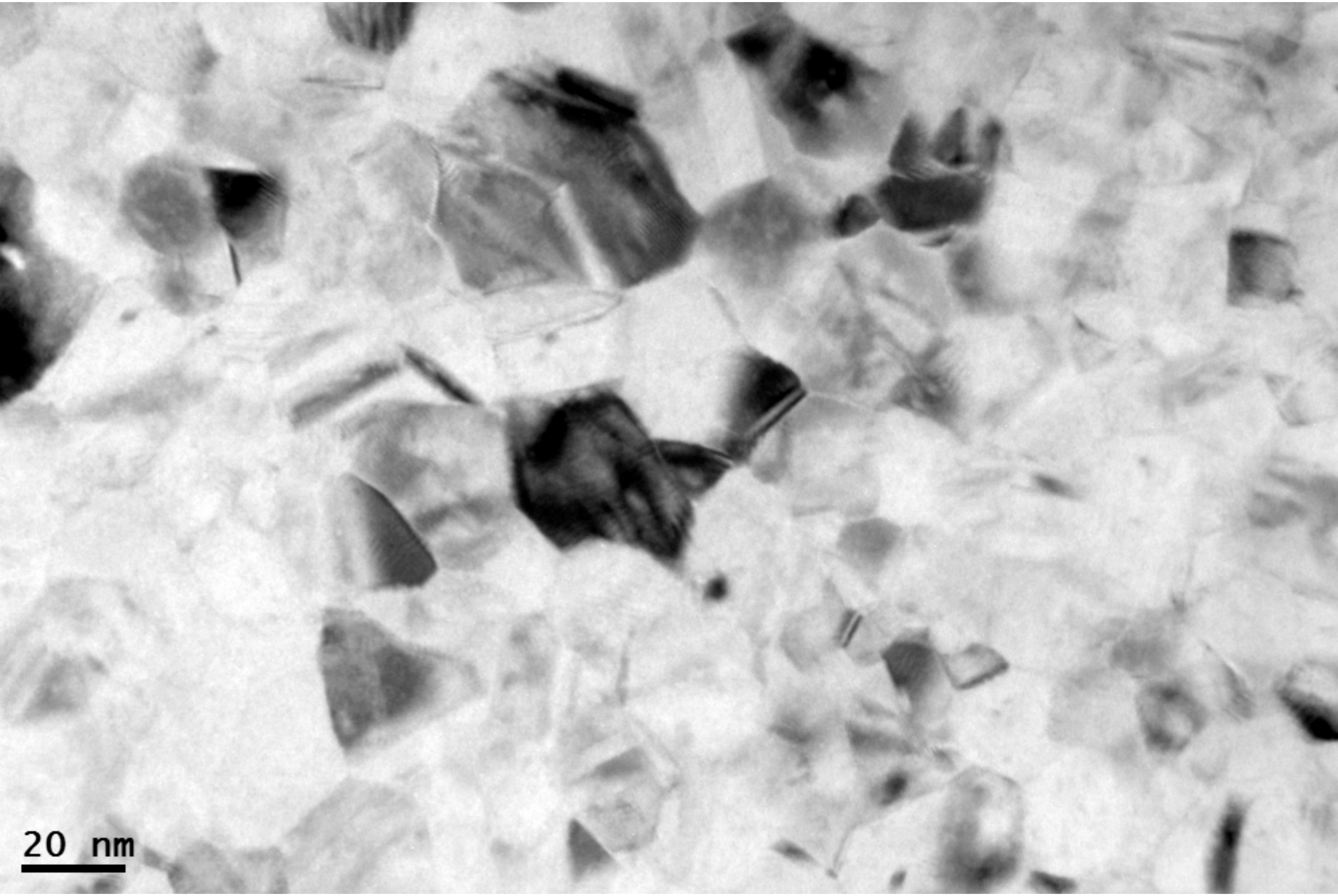
- This system was considered because the as-irradiated samples display disordered grain boundaries. The hope was to contrast this against ordered grain boundaries, and equilibrium GB complexions.
- Unfortunately, the boundaries recrystallize during the diffusion annealing
- However, they are still good reference for samples for: (a - the as deposited film) a system with a non-equilibrium GB composition that is reasonably high, and (b - the as irradiated sample) a system that has a relatively low (close equilibrium) segregation level.



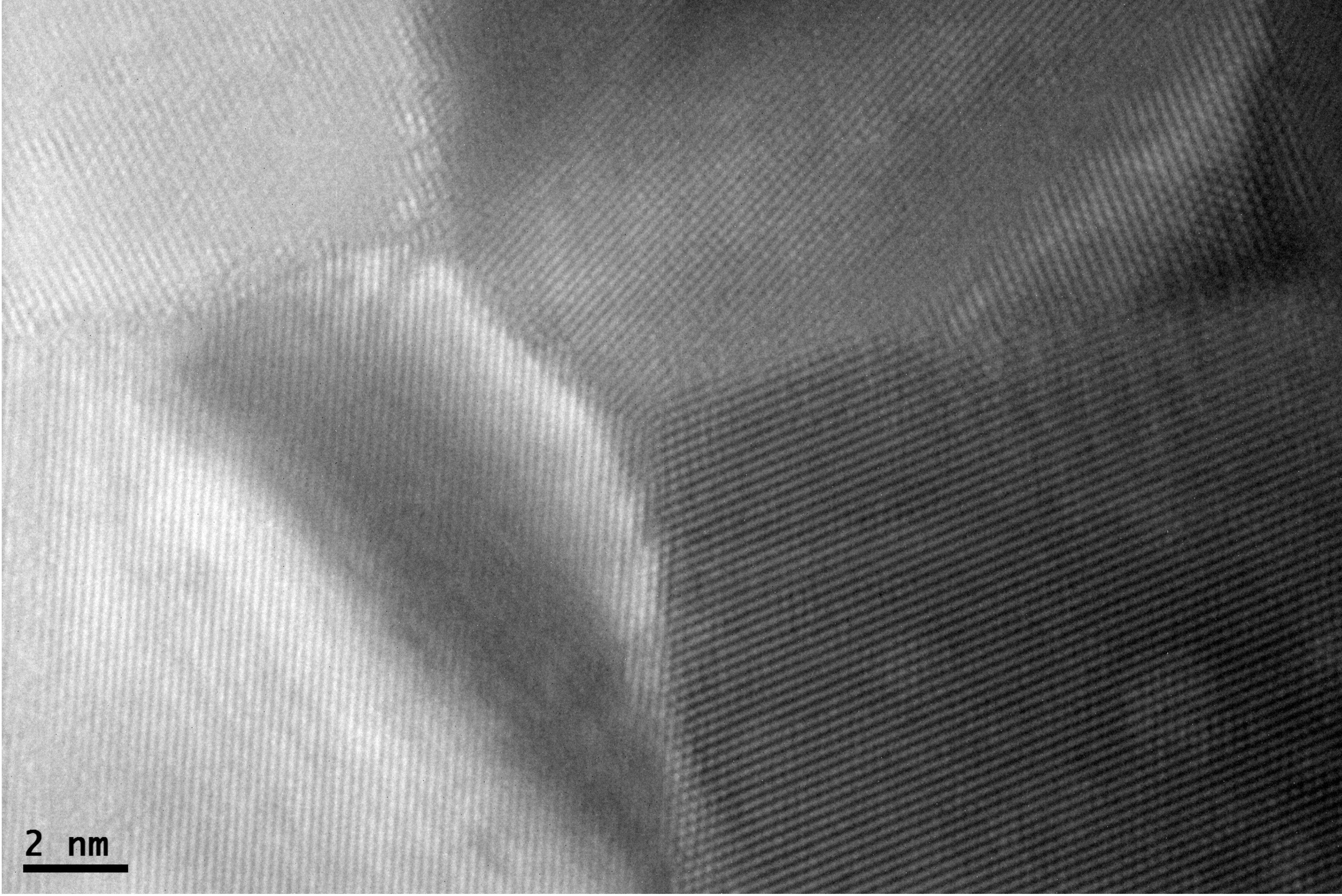
Au coating on Cu-W (de&irrad) annealed at three temperatures



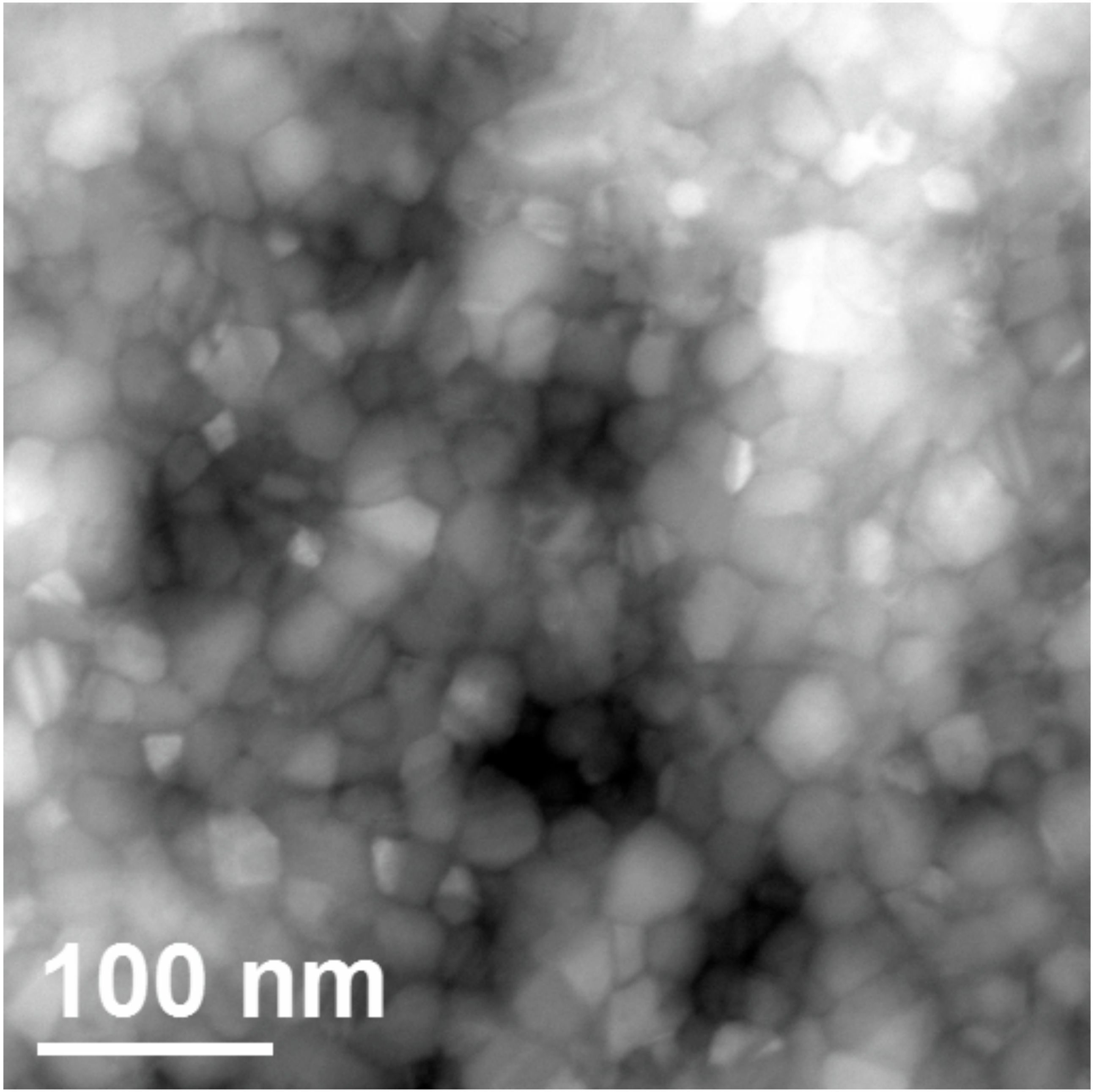
Cu-1%W as-deposited: grain size ~20nm



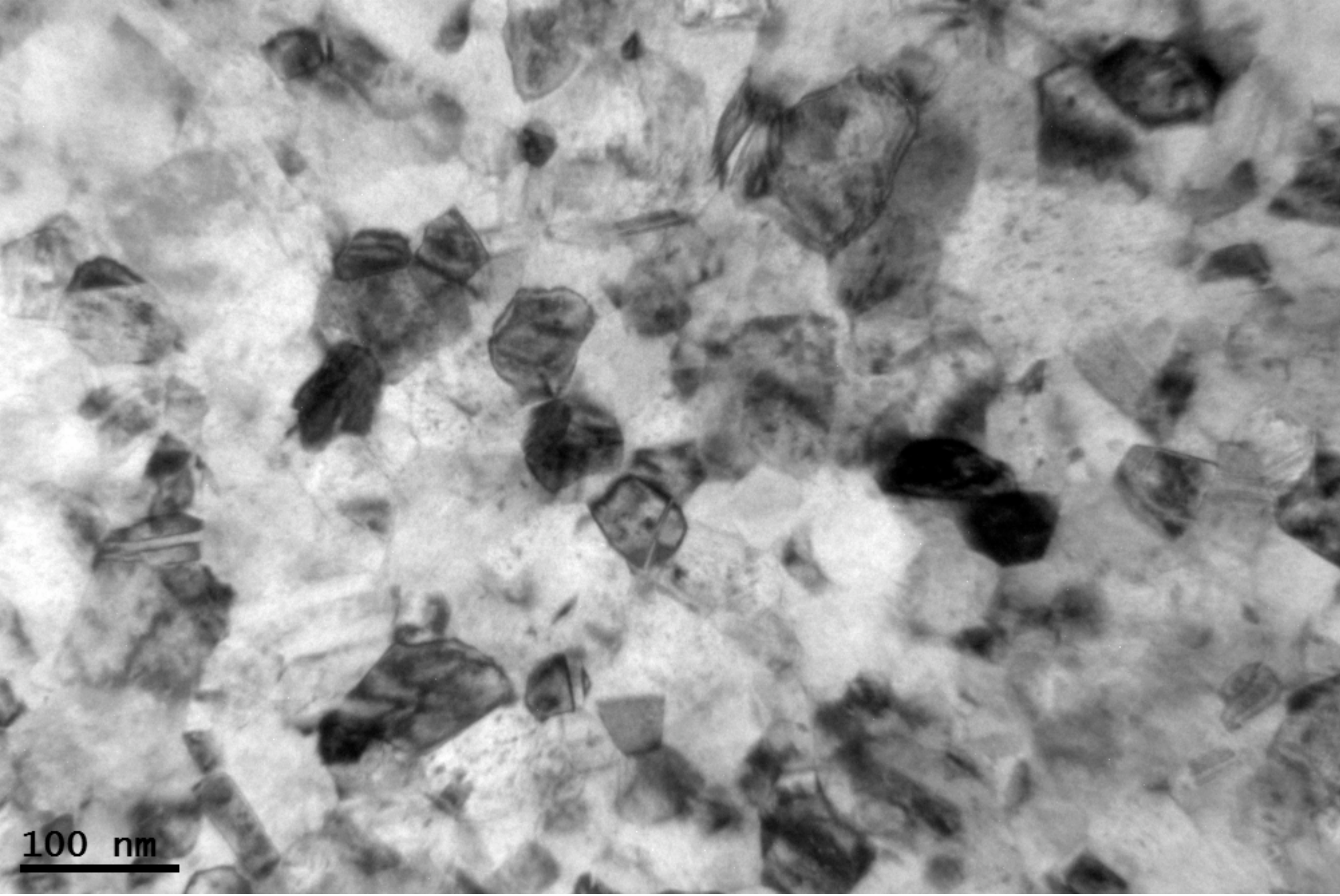
Cu-1%W as-deposited: grain size ~20nm



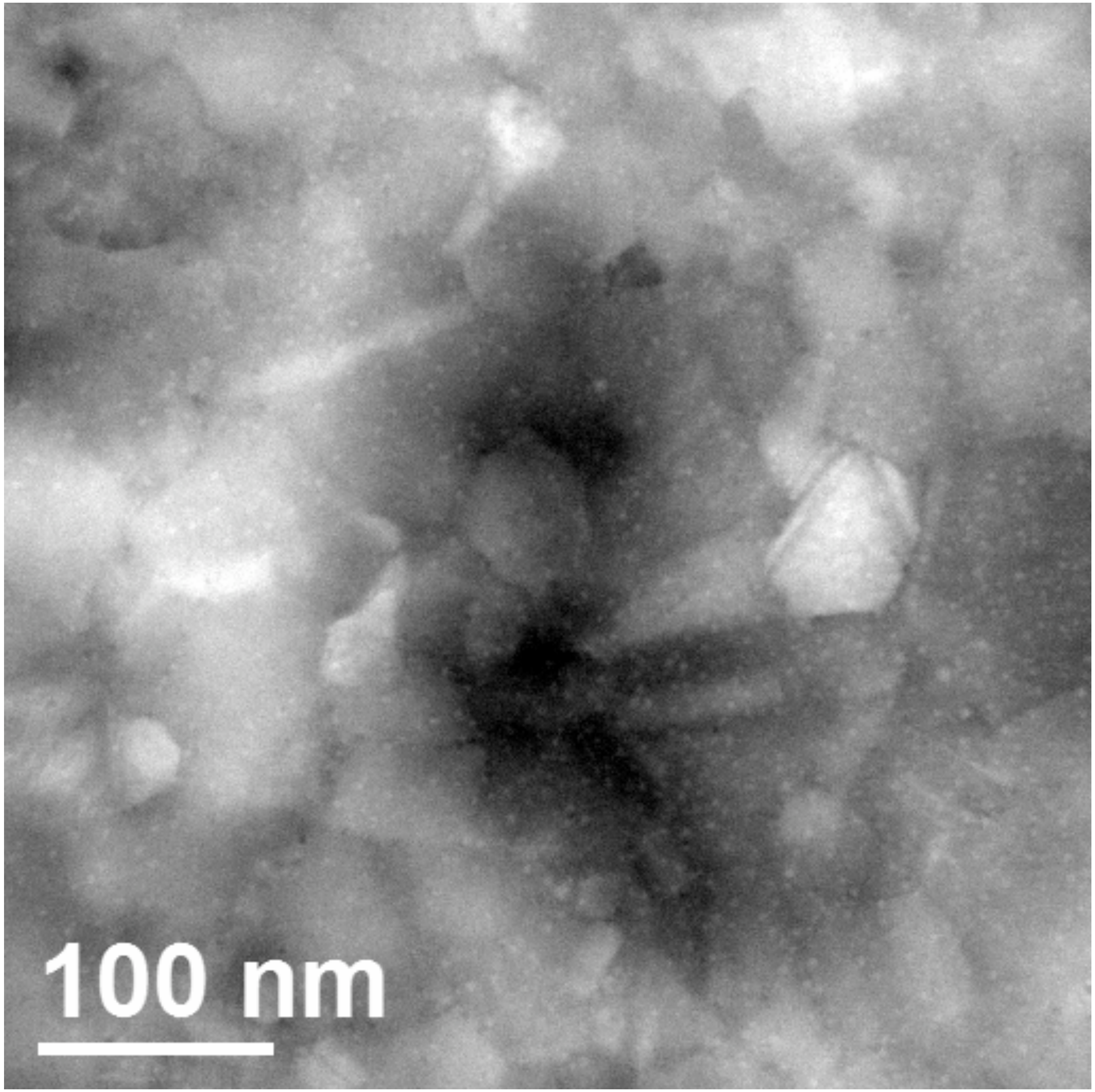
Grain boundary width ~1nm, with various crystallography orientations



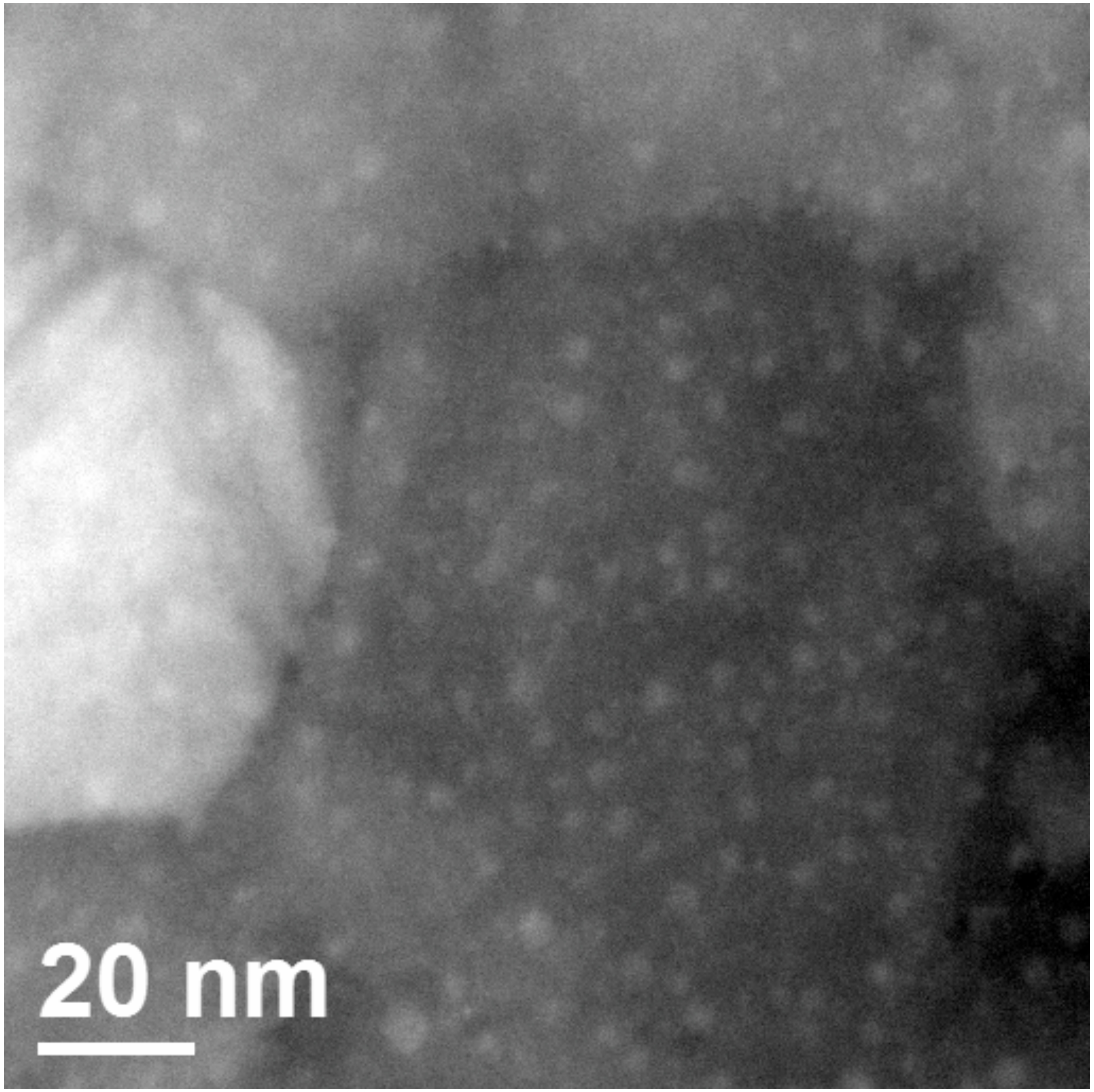
(Z-contrast) Cu-1%W 473K annealed (No obvious grain growth and precipitation)



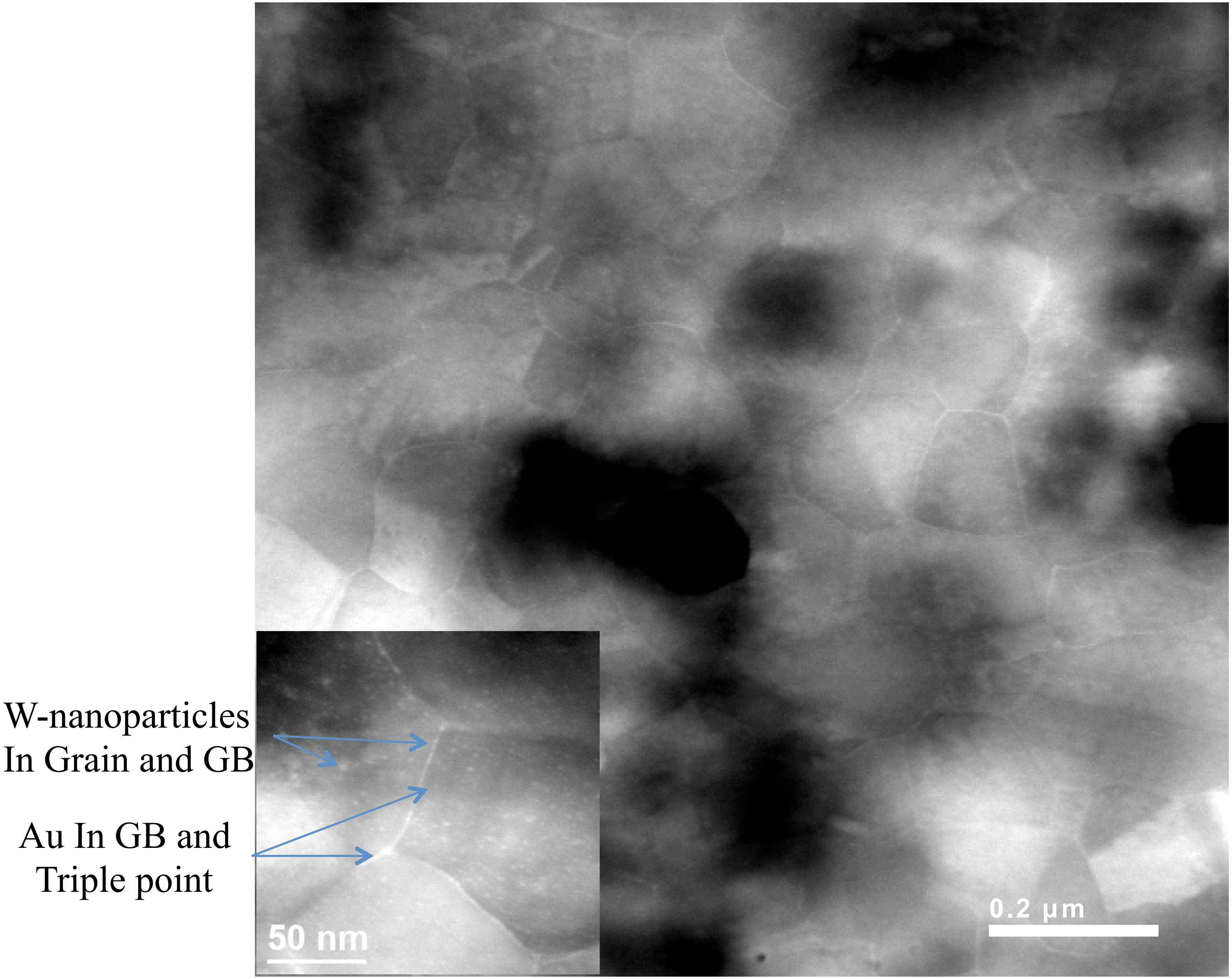
Irradiated Cu-1%W, grain growth ~80nm and lots of nano-precipitations (black spots)



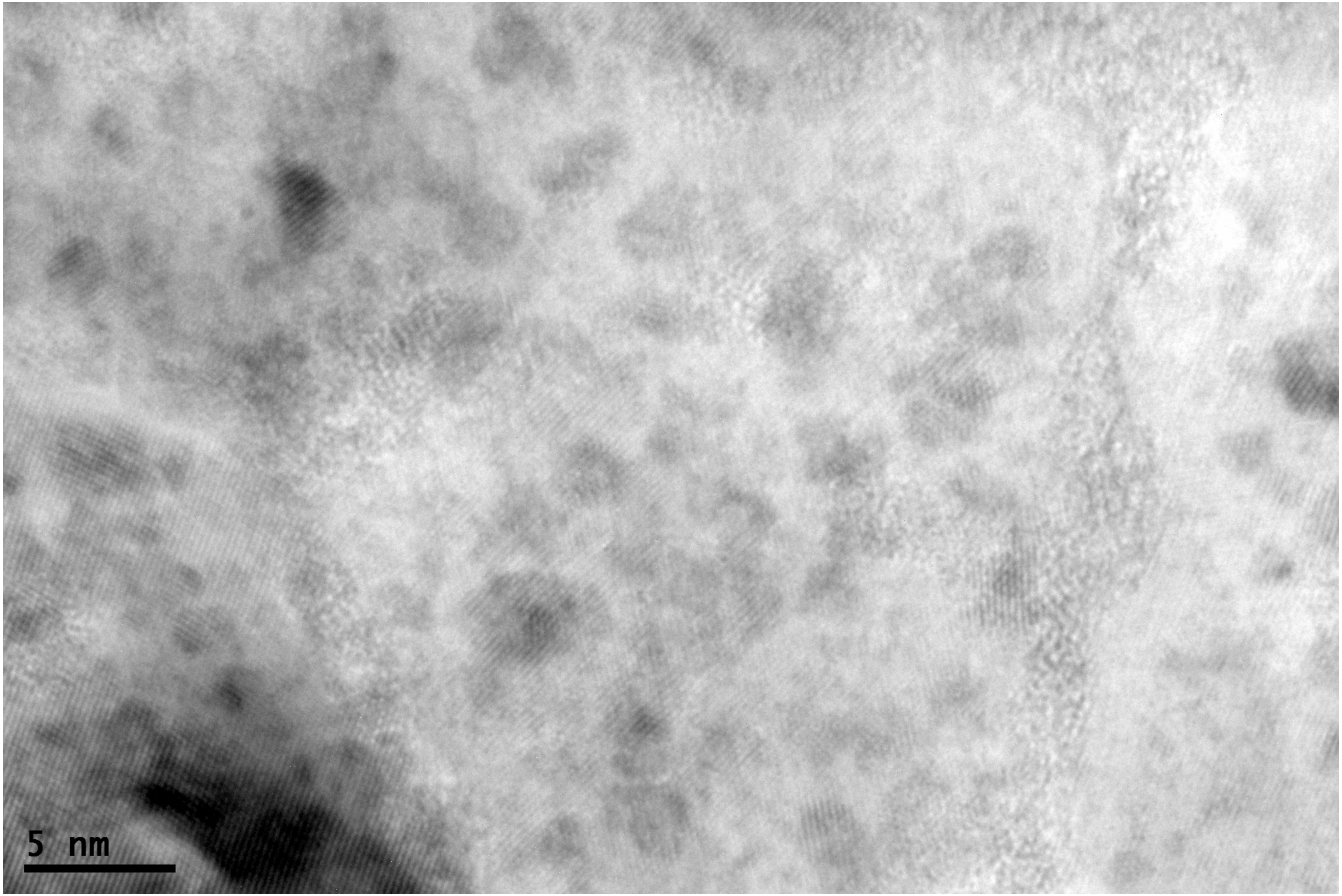
(Z-contrast) Irradiated Cu-1%W, high density of W-nanoparticles and dark GB



Bright spot: Ion irradiation induced W-nanoparticles distribute uniformly

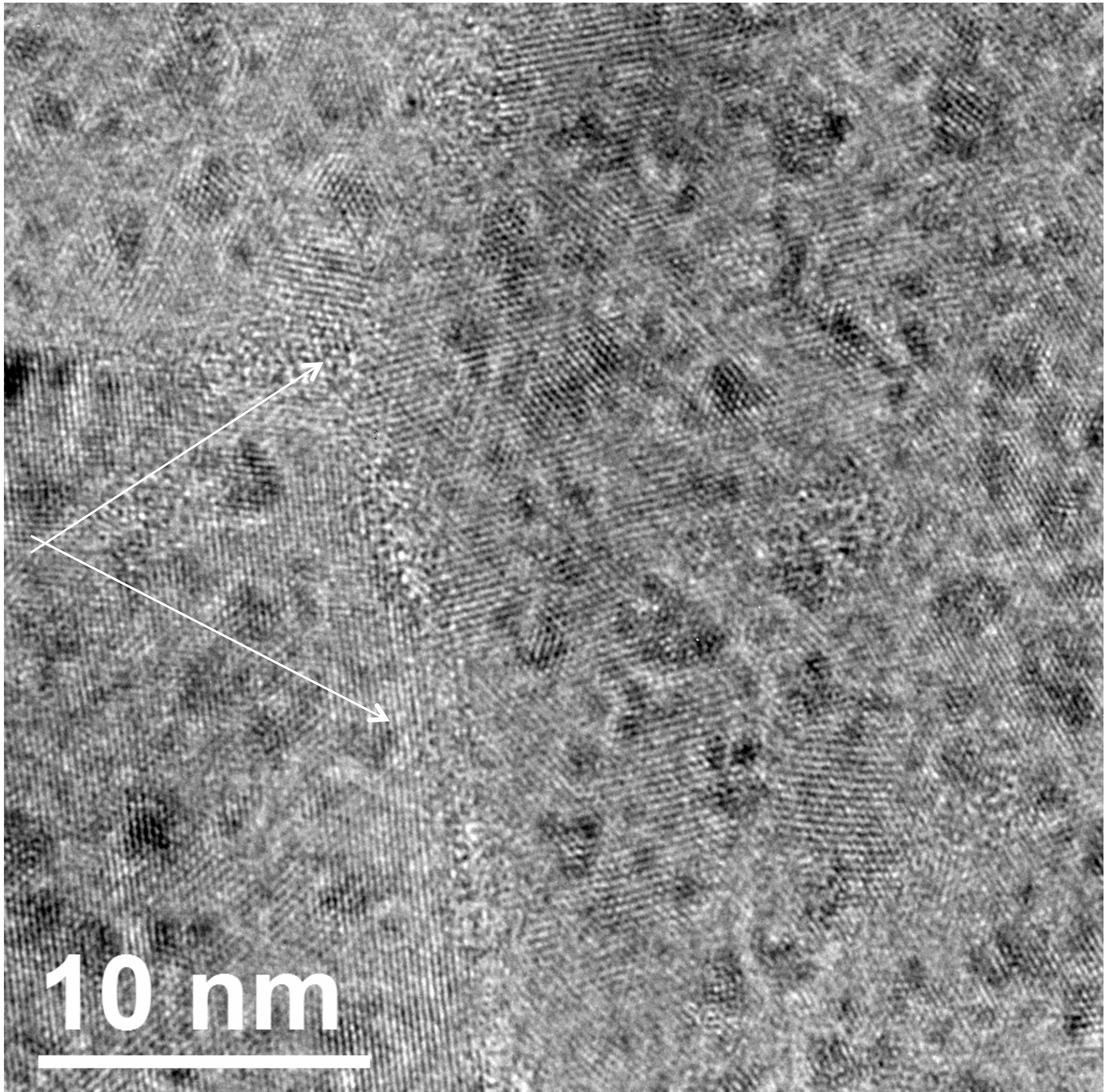


Nano-type C: (Z-contrast) Au diffusion along irradiated Cu-1%W GB
(bright spot: W-nanoparticles, bright GB: Au-enriched)

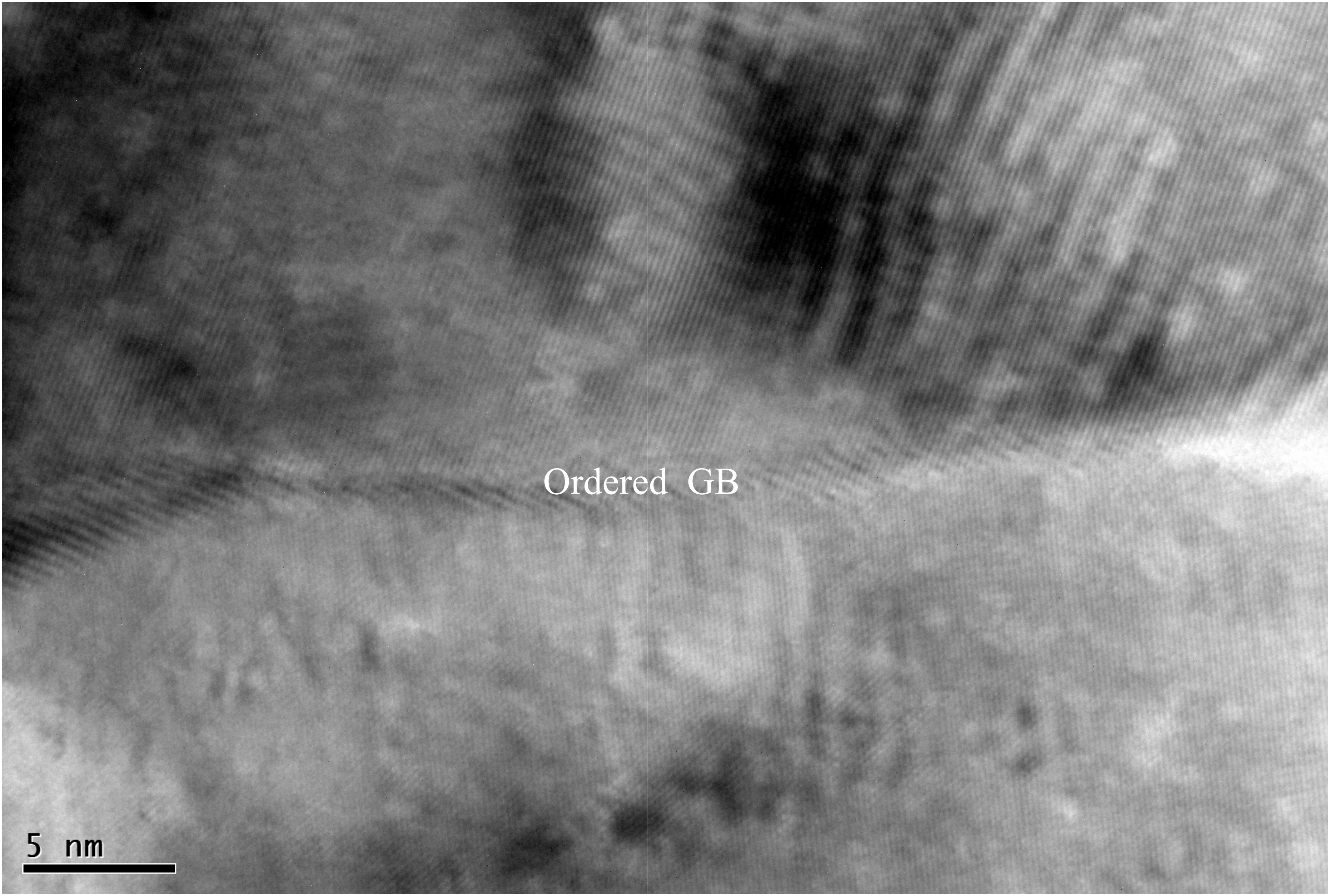


Cu-1%W after irradiation GB in Disorder Structure

Amorphous GB

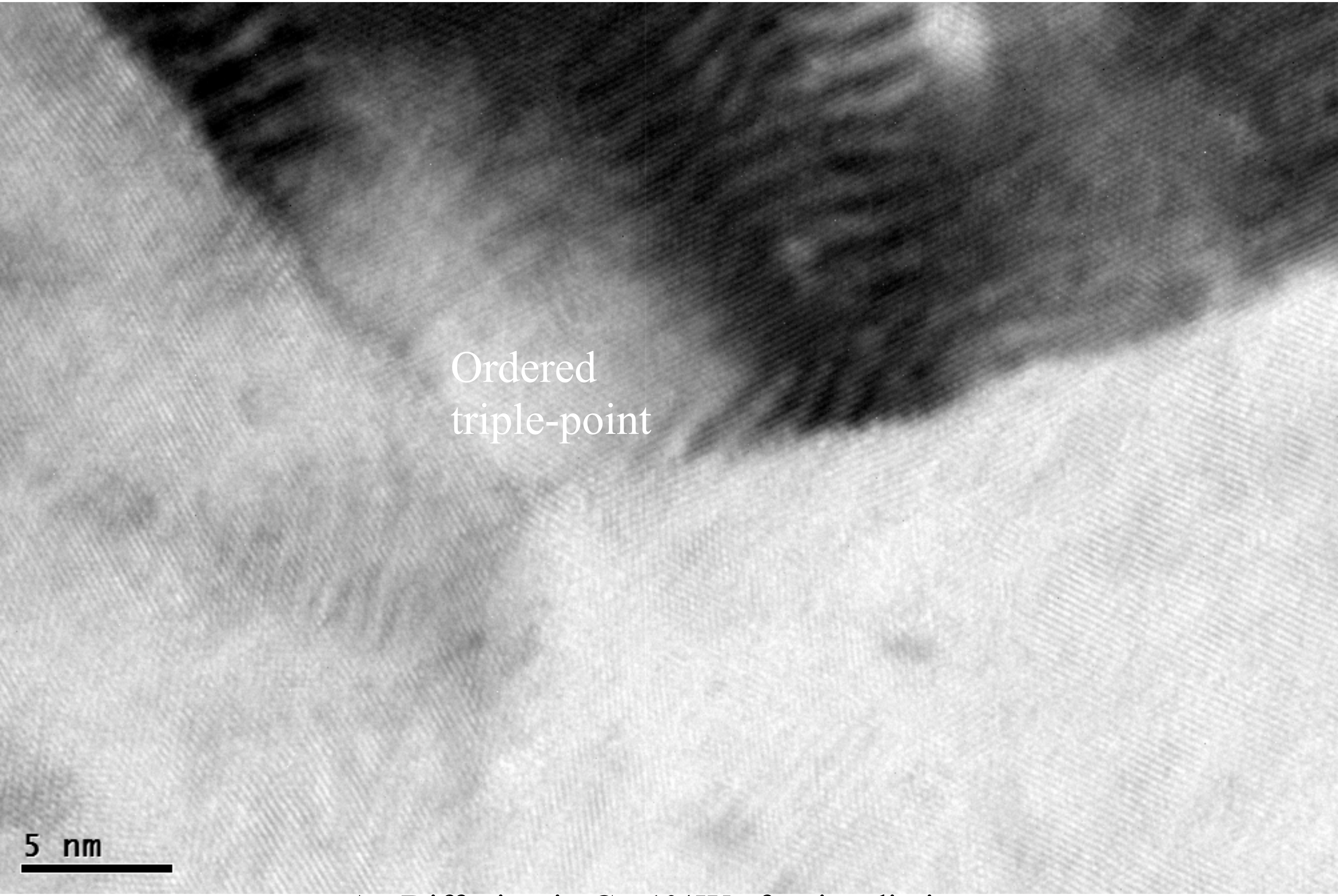


Cu-1%W after irradiation GB in Disorder Structure

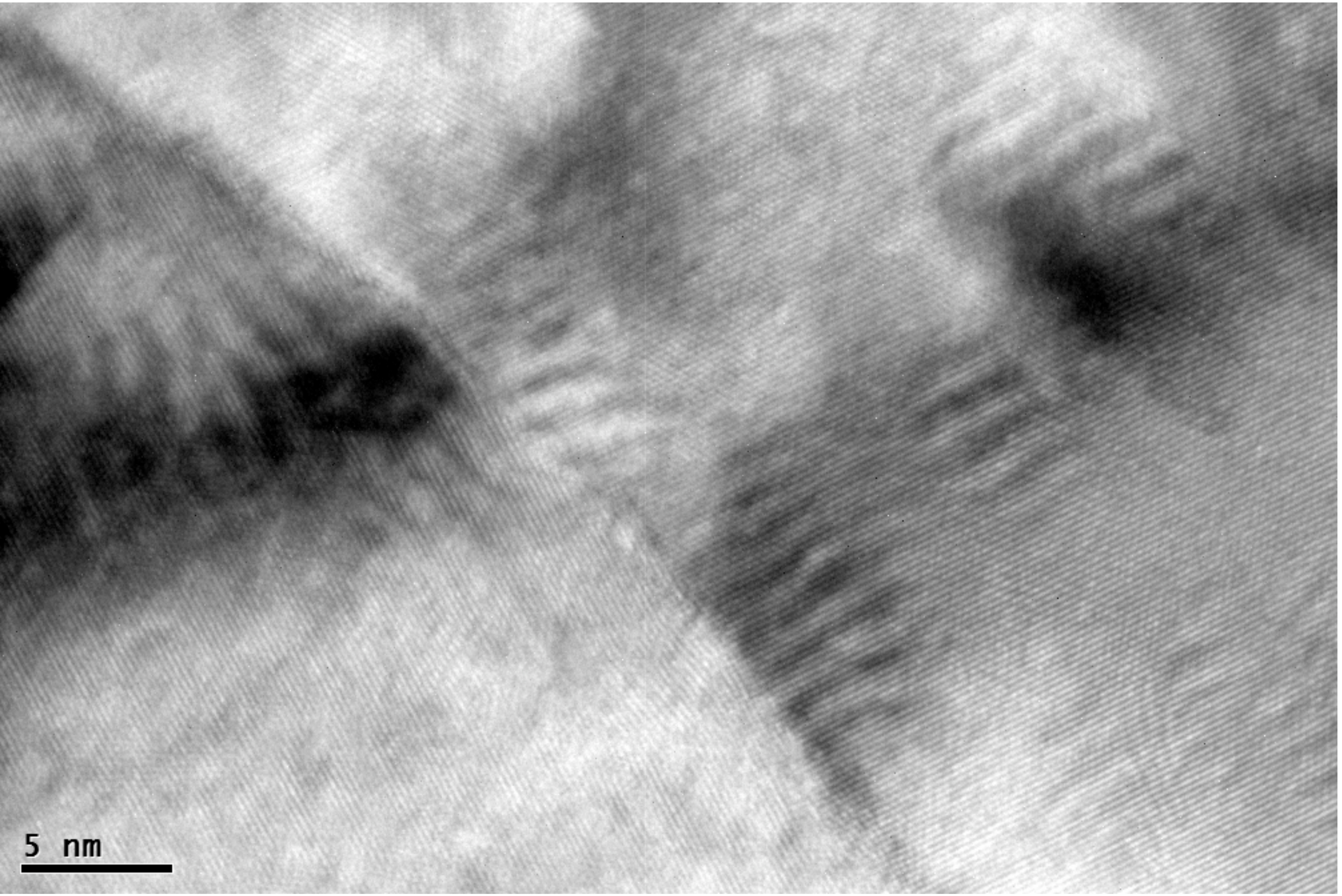


Au Diffusion in Cu-1%W after irradiation
at 473K GB in Ordered Structure

Au Diffusion in Cu-1%W after irradiation
at 473K GB in Ordered Structure



Au Diffusion in Cu-1%W after irradiation
at 373K GB in Ordered Structure



Au Diffusion in Cu-1%W after irradiation
at 373K GB in Ordered Structure