Correlation of Macroscopic and Microscopic Properties of Tungsten Doped Nanocrystalline Diamond Coatings

25thTarget Fabrication Specialists Meeting

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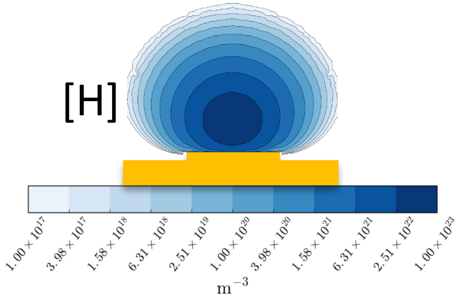
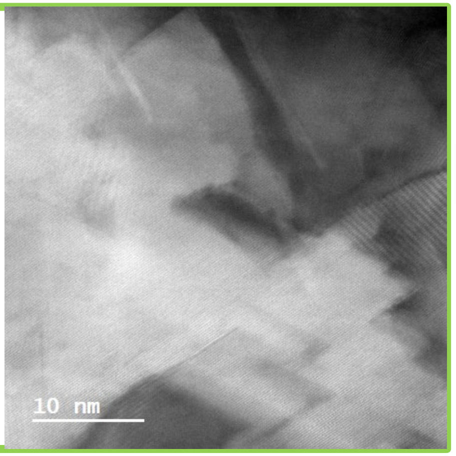
June 28, 2024

Correlating and Tuning Macroscopic and Microscopic Properties Relevant for Target Fabrication and Performance

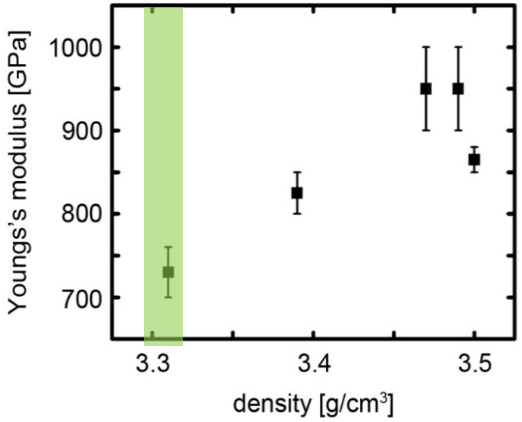
Process parameters
- Pressure
- MW power
- Gas composition
-



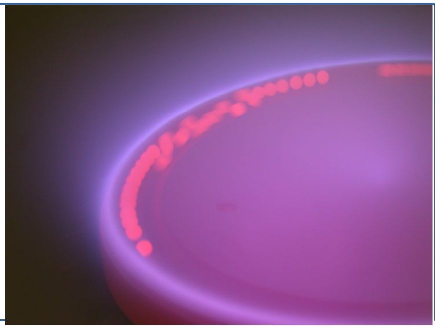
Microscopic diamond properties
- Grain size
- W-doping
- sp^2-C content
- H content
- ……



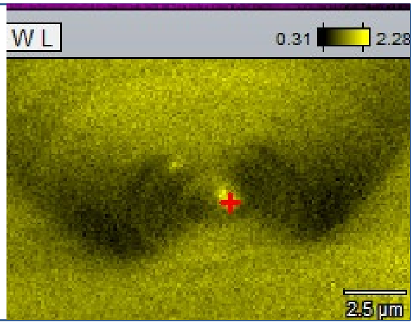
Macroscopic diamond properties
- Density
- IR transparency
- Resistivity
- Youngs modulus
- …….



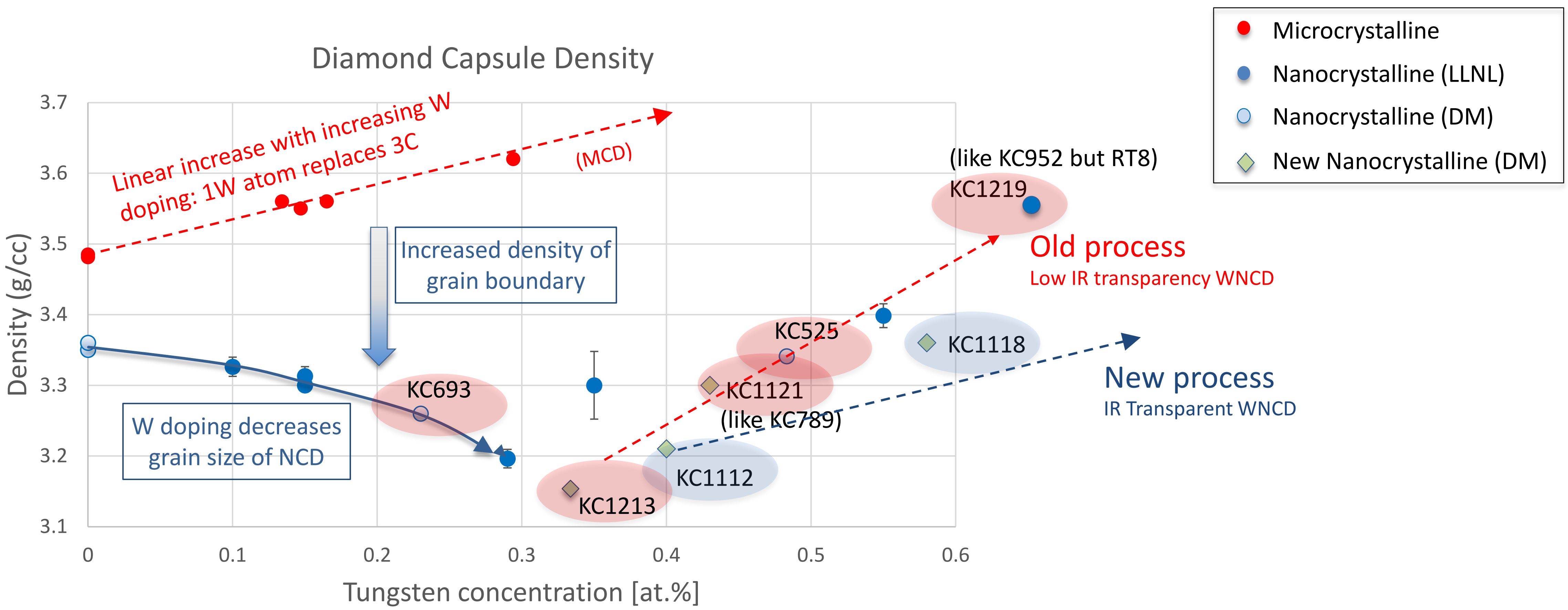
Hardware
- Gas inlet
- Agitation
- Racetrack
- …….



Defects
- Voids
- High Z
- Petal defects
- …….

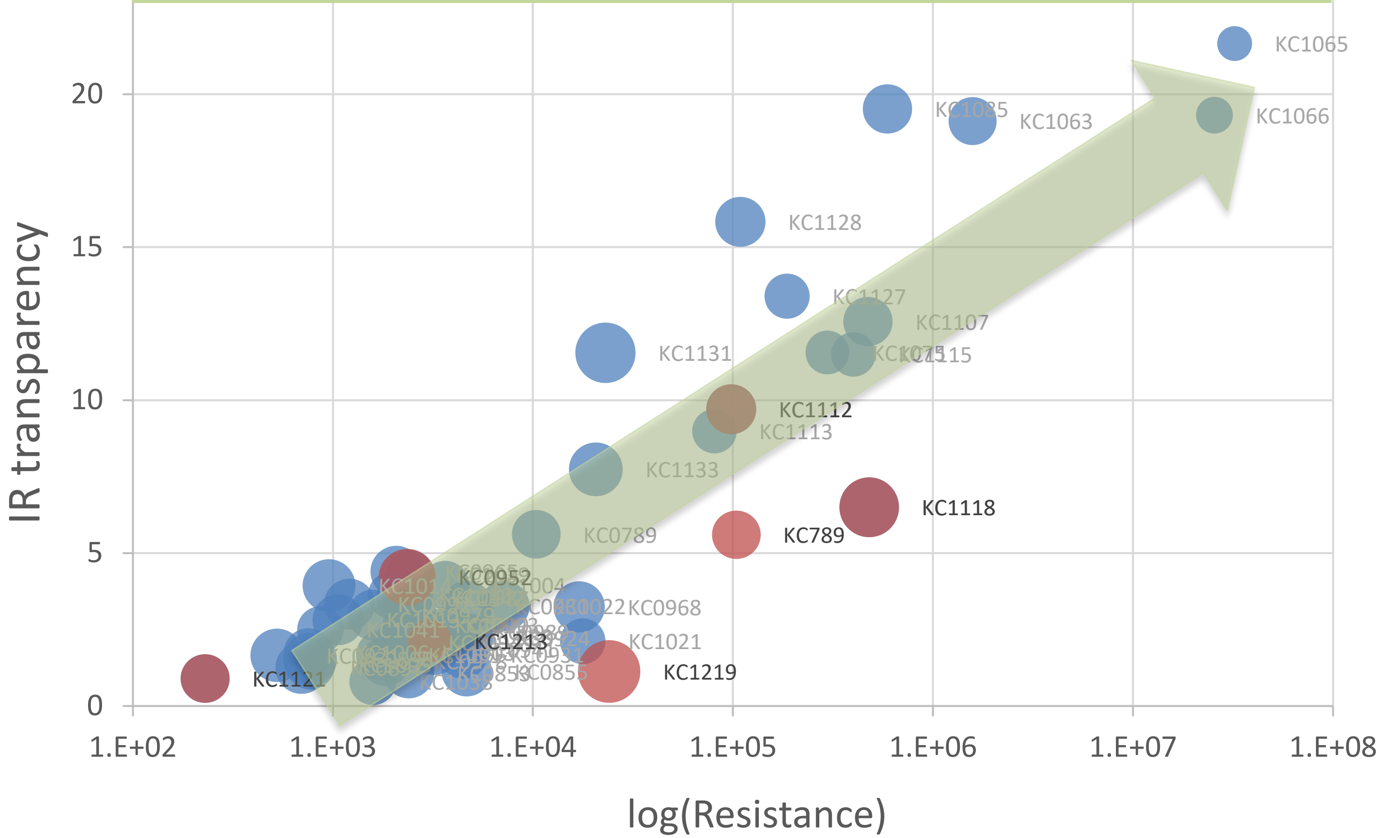


Density – W doping correlation of W-NCD suggests grain size refinement with increasing W concentration

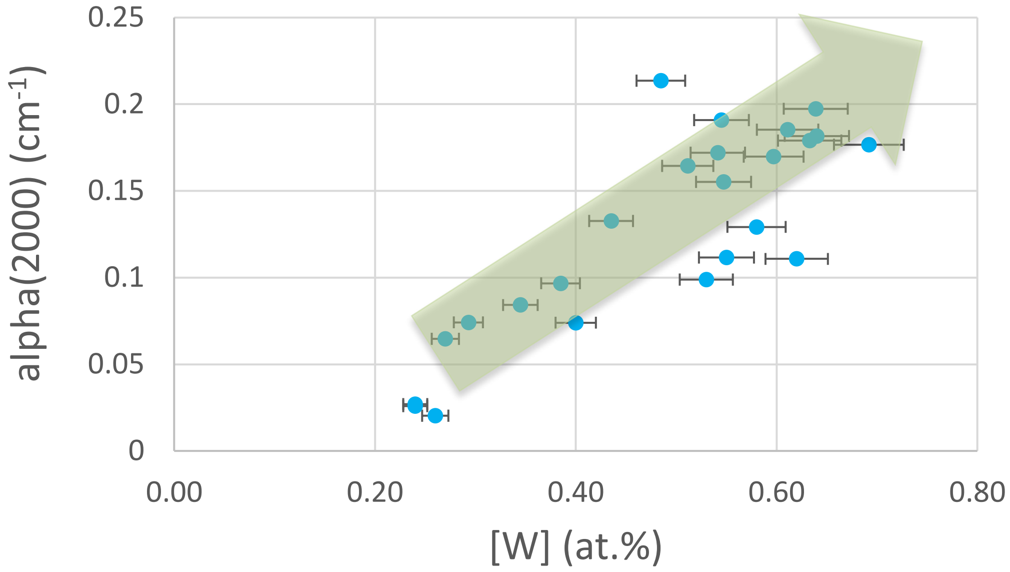


Macroscopic properties of W-NCD seem to be dominated by graphitic carbon content

Increasing resistance with increasing IR transparency



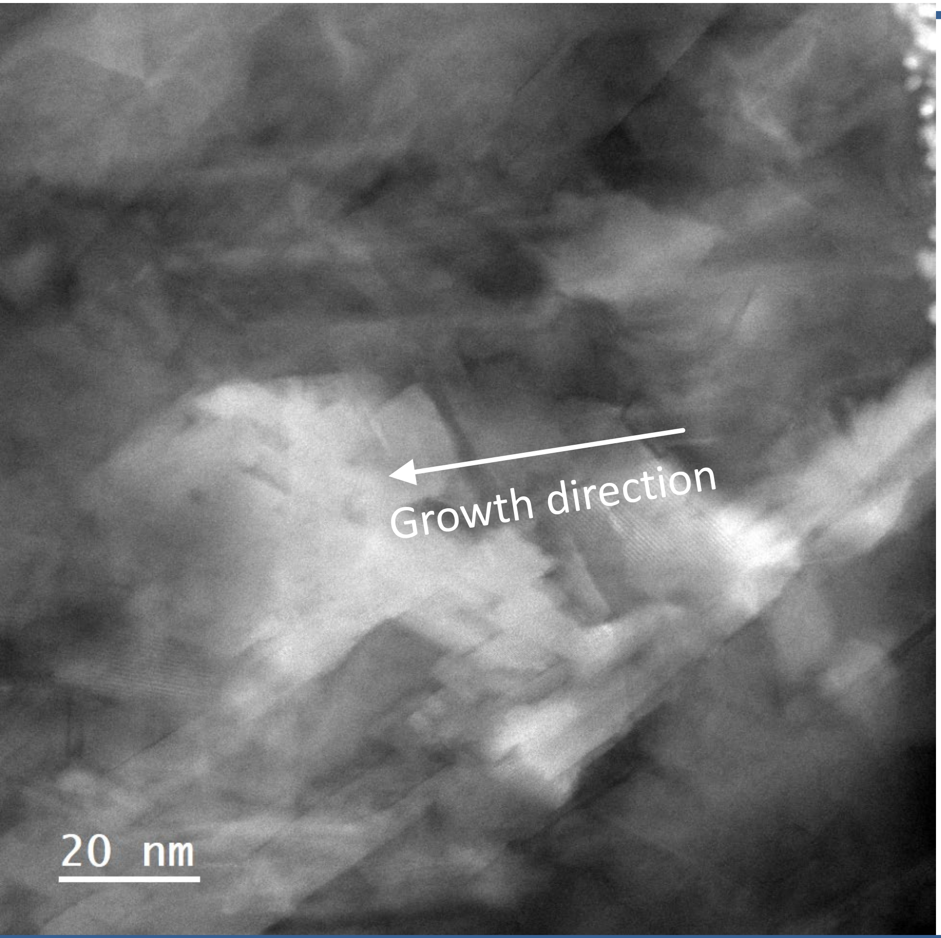
IR absorption coefficient increases with increasing [W]

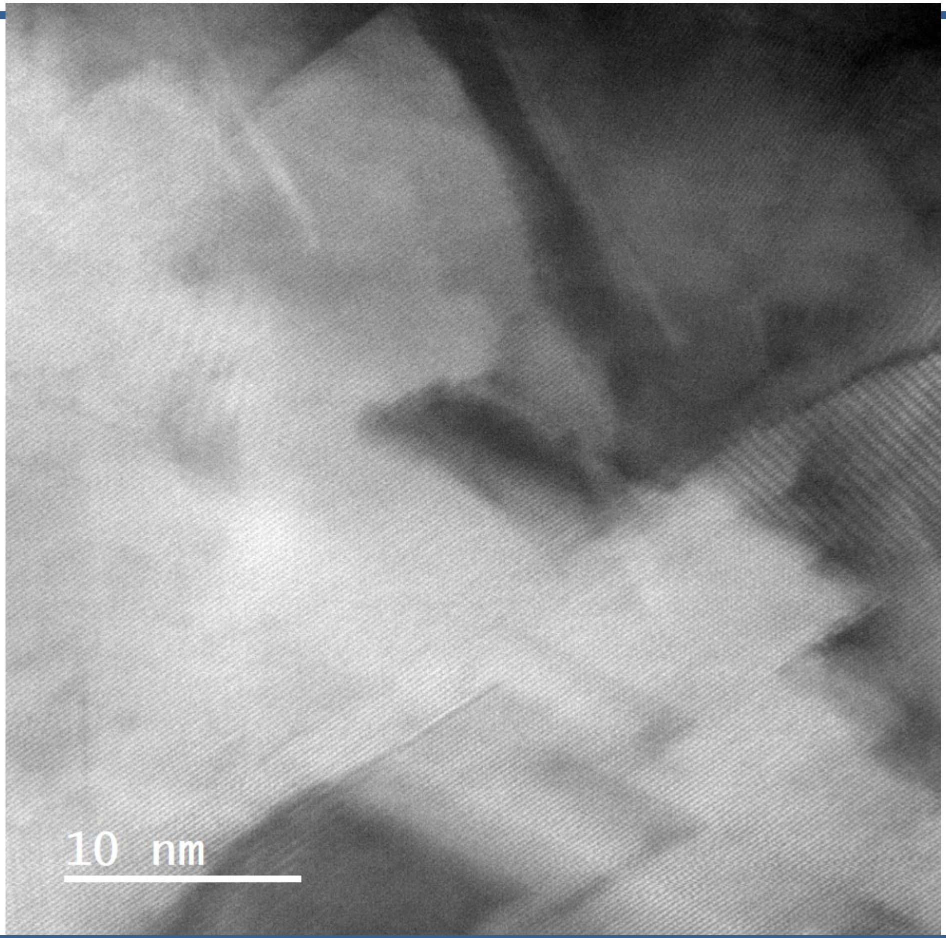


α-[W] correlation holds only for a fixed CVD recipe

- IR transparence increases with increasing resistance
- IR Absorption coefficient increases with increasing [W]

TEM confirms well-defined nanoscale grain structure





HAADF STEM (UPenn): KC952 /undoped region

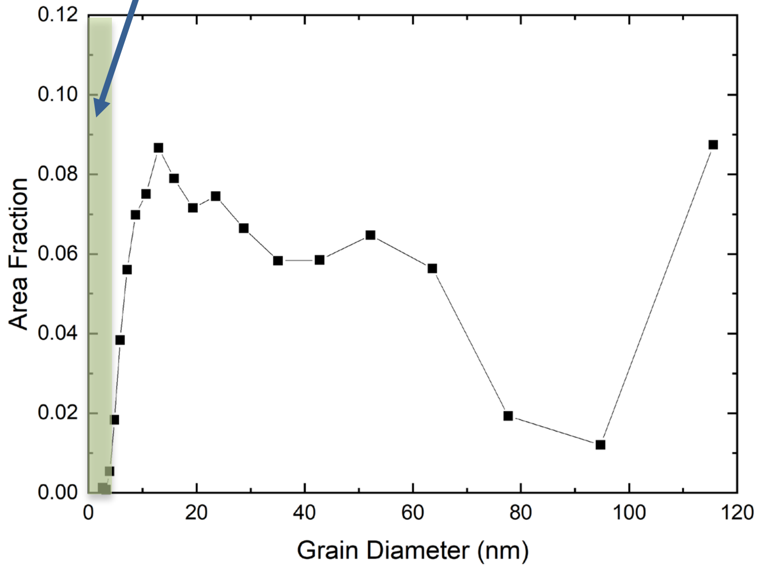
Contrast provided by Bragg diffraction (camera length 4 cm)

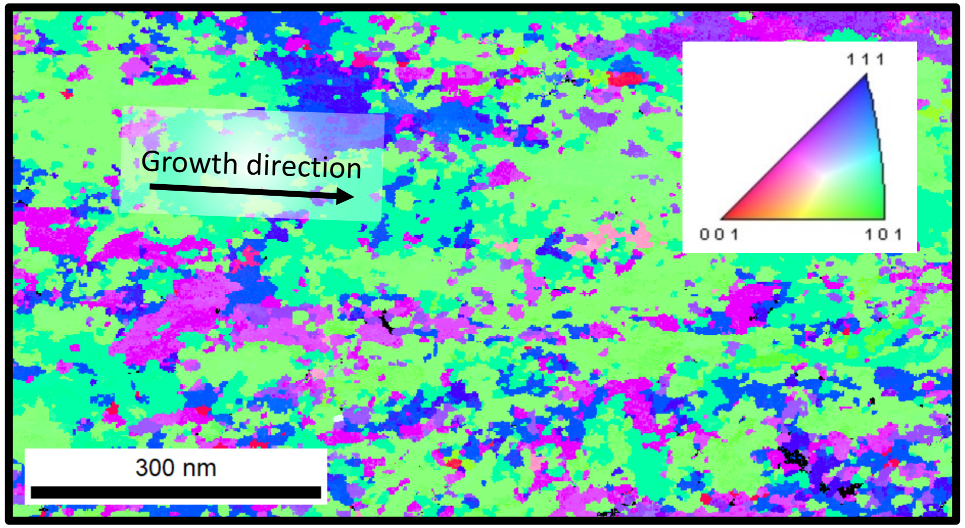
- Well defined crystalline sub-100 nm diamond grains
- Large elongated regions with similar grain orientation (texture)

Diffraction-based TEM techniques confirm nanoscale grain structure and the presence of texture

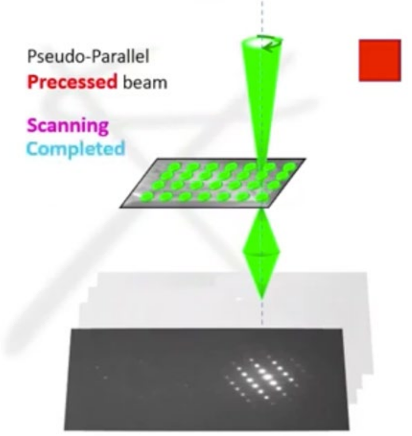
KC1112
KC1063 duplicate
New process
0.43 at.% W

software default "clean-up" routine filters out very small, sub ~5nm grains





Scanning Precession Electron Diffraction (SPED)



1.5 nm pixel size

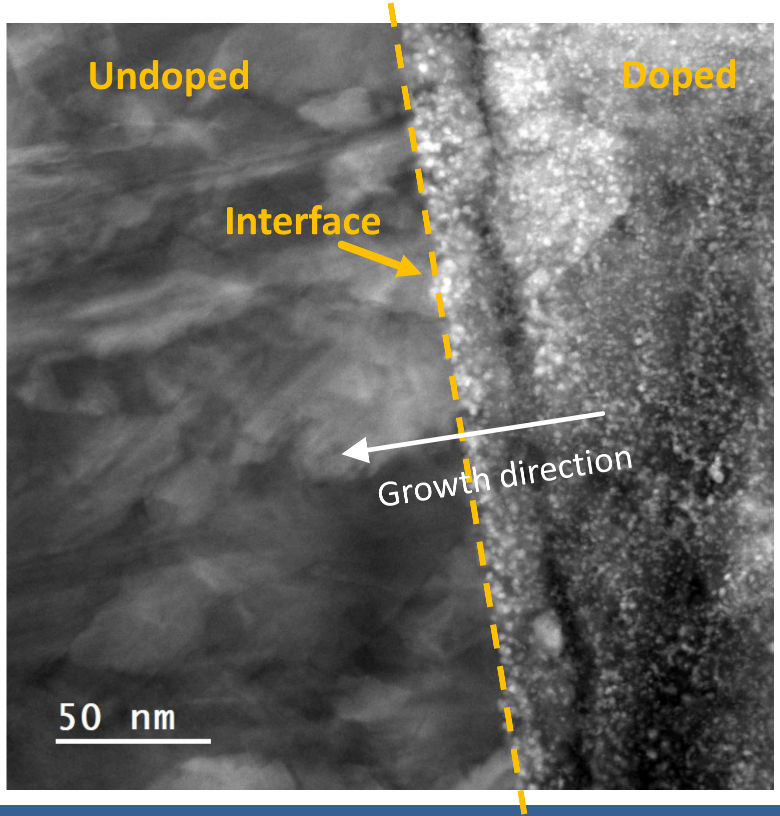
Tony Li, LLNL

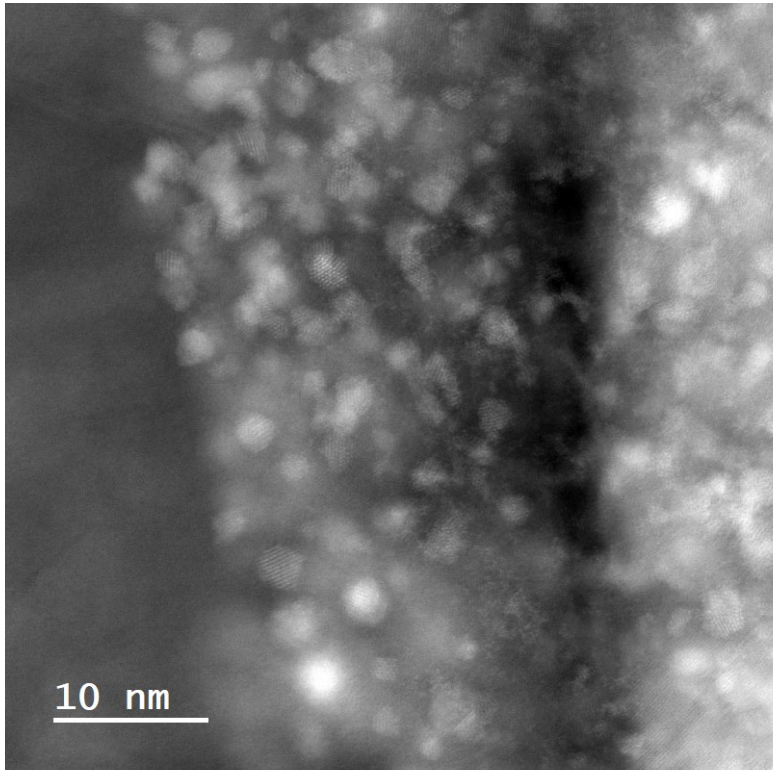
- Elongated grains in growth direction
- Volume on W-NCD dominated by sub-100 nm grains with a peak around 10 nm
- Low angle grain boundaries seem to dominate (associated with lower local density)
- Analysis currently limited by the thickness of available TEM lamellas

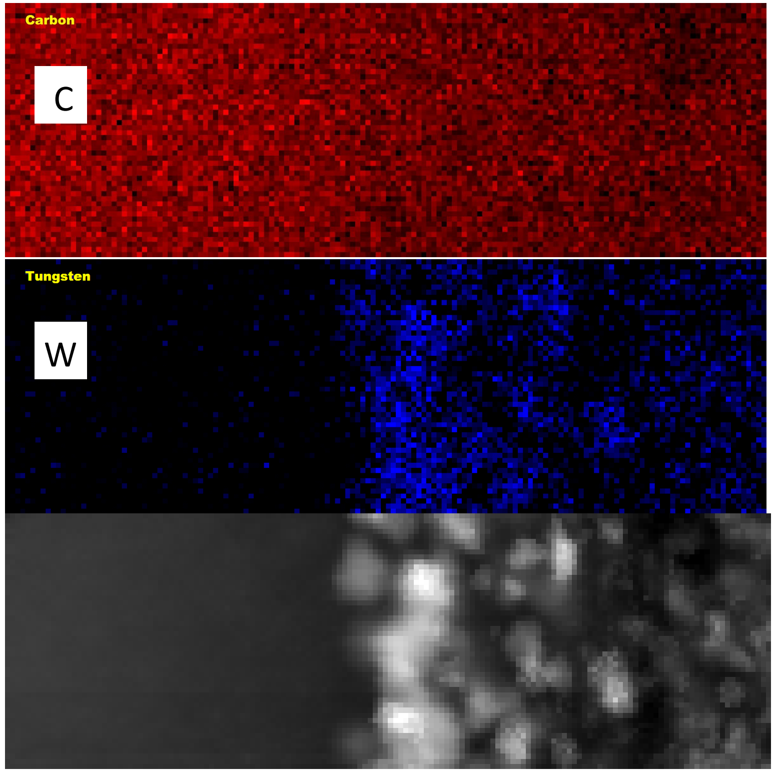
Nanoscale W precipitates observed in the W-NCD layer

KC952 (0.56 at.% W) / old process

HAADF STEM / UPenn



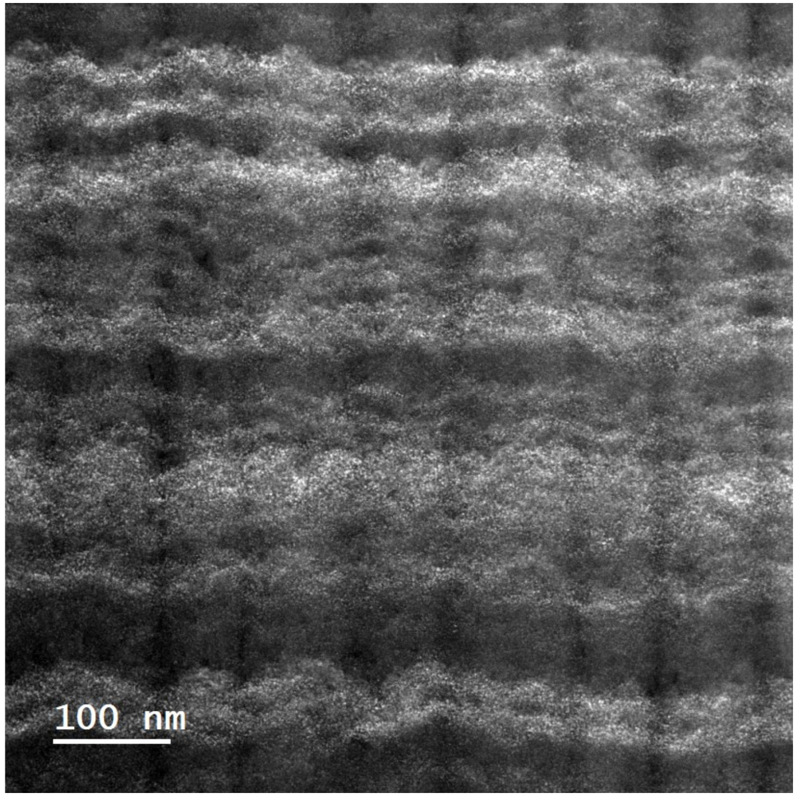


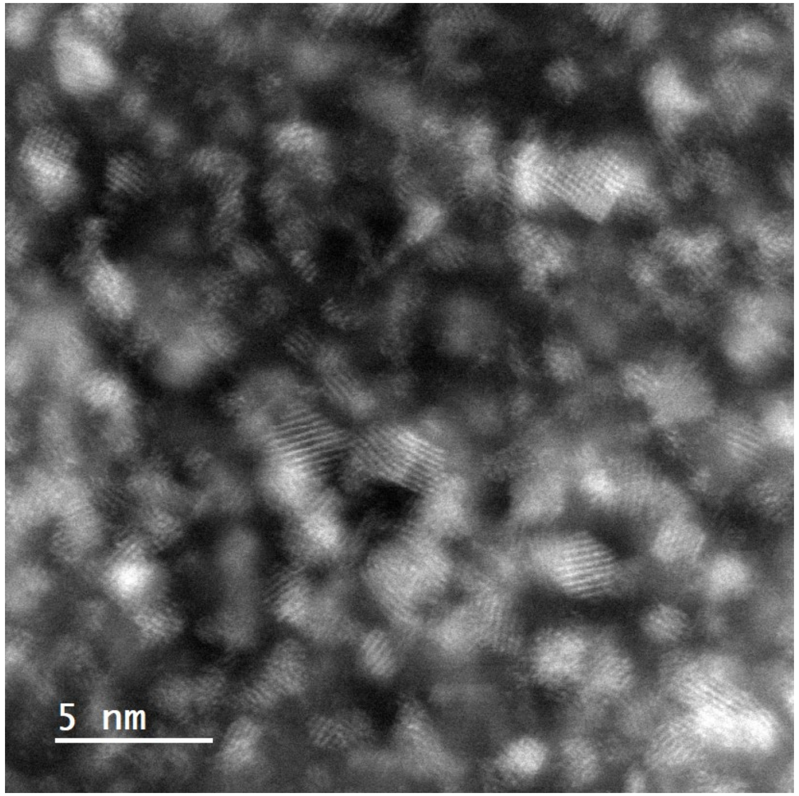


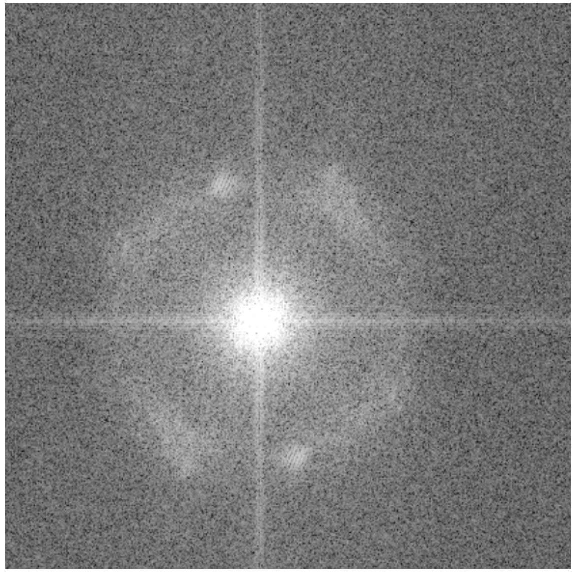
- Grain size of NCD > grain size of WNCD
- Elongated grains in grow direction, equiaxed grains perpendicular to growth direction
- Small (< 5 nm) WC nanoparticles in doped region

Nonuniform tungsten distribution: Banding and tungsten carbide nanoprecipitates

KC1112
KC1063 duplicate
(plus improved agitation)
New process
0.43 at.% W





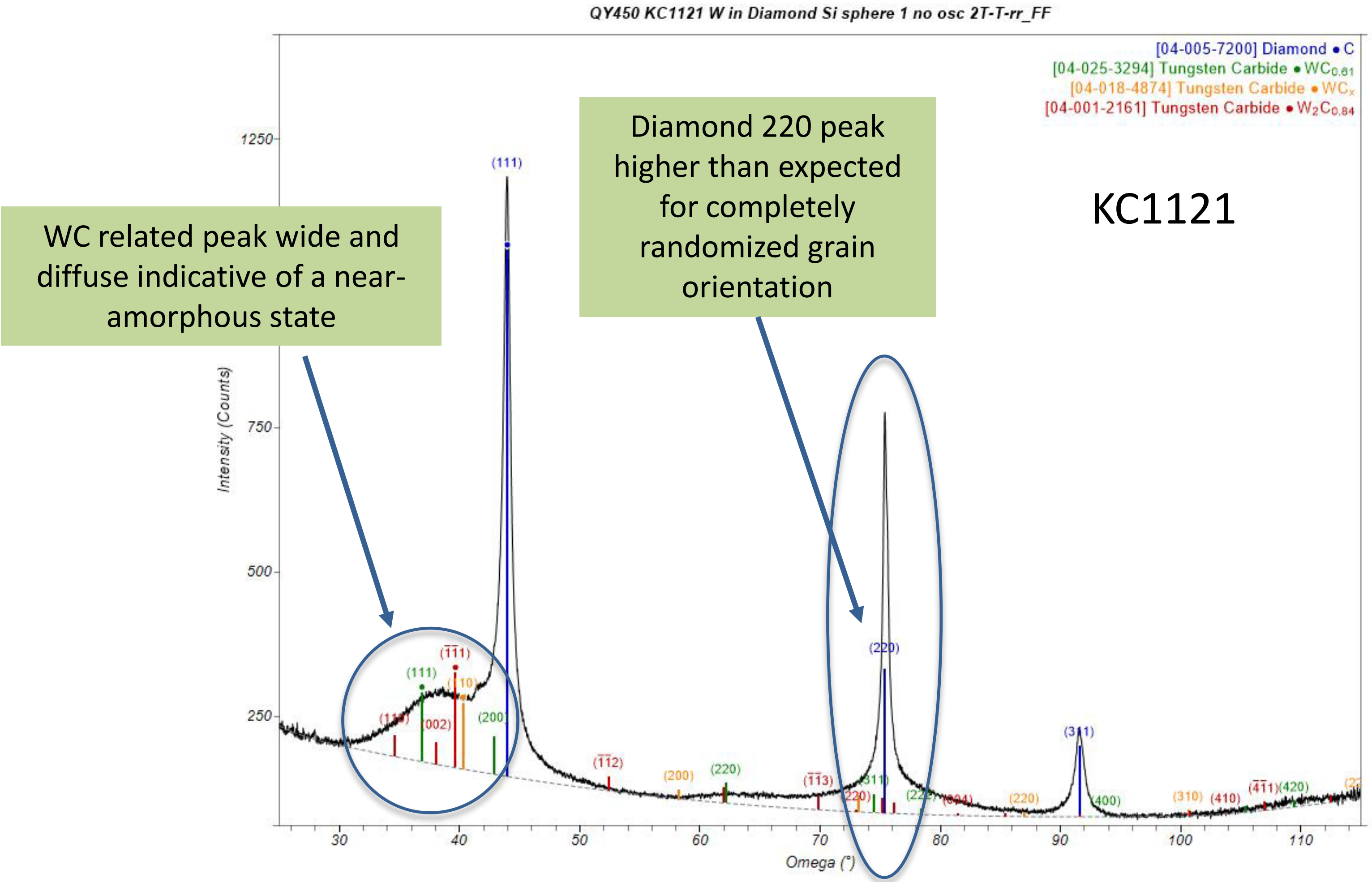


Diffuse FFT consistent with small size of the WC nanoparticles / mixture of different WC_x phases

HAADF STEM (UPenn):
Camera Length = 2 cm
Contrast dominated to Rutherford scattering

- Banding reflects local variation of WC particle density (shell agitation related)
- The WC nanoparticles have a diameter of 1-3 nm
- WC lattice fringe spacing ~ 2.4 Å
  - ➢ Consistent with 111 plane spacing of cubic WC ($4.39 Å/\sqrt{3} = 2.53Å$)
  - ➢ But can not rule out coexistence of orthorhombic W_2C phase: (200) plane spacing 2.36 Å

XRD confirms the presence of WC precipitates and texture

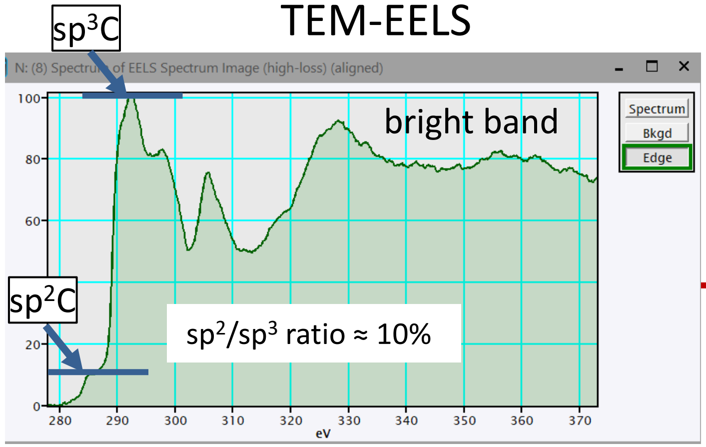


XRD (EAG)

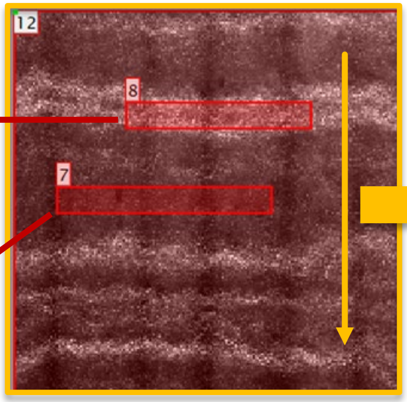
- Weak 220 texture (fast growth direction): Old process seems to result in a slightly higher texture than new process
- ~25% of the incorporated W is in the form of small WC particles embedded in the diamond matrix

Higher sp^2-C concentration in bright (WC-rich) bands

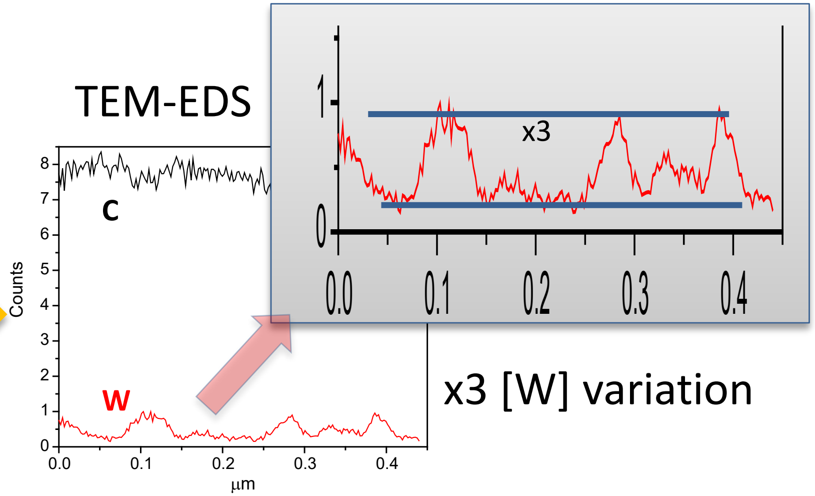
TEM-EELS



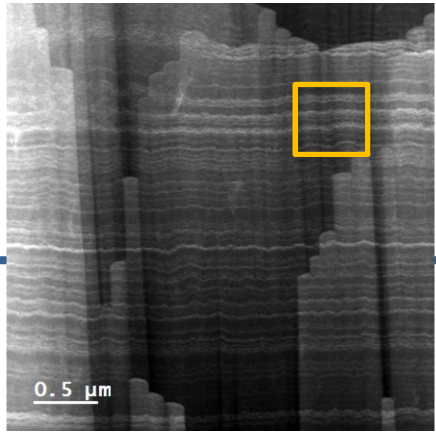
KC1112
KC1063 duplicate
(plus improved agitation)
New process
0.43 at.% W

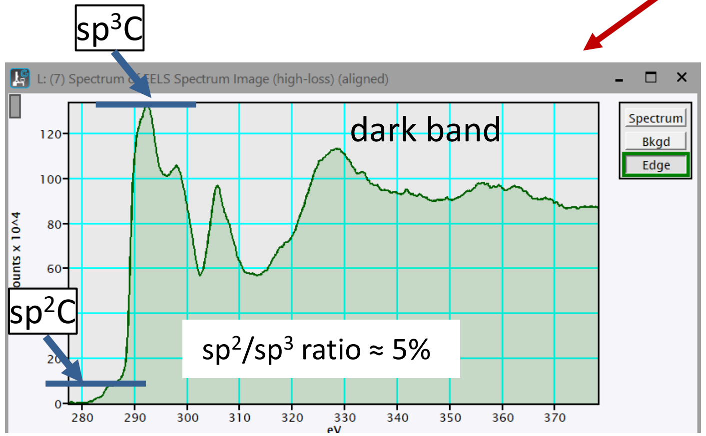


TEM-EDS



x3 [W] variation

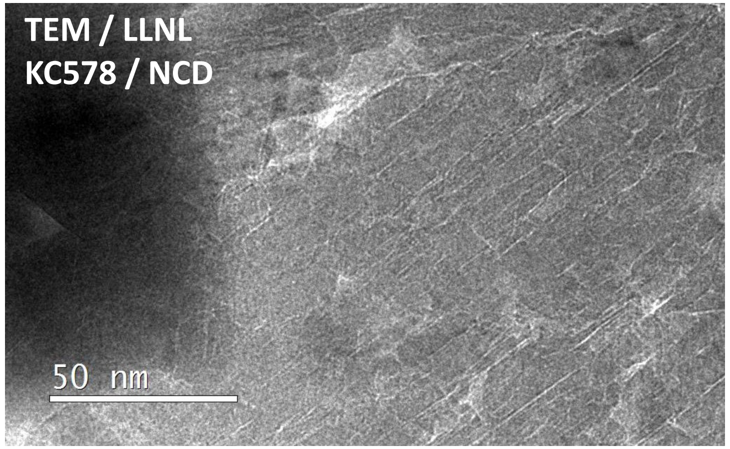




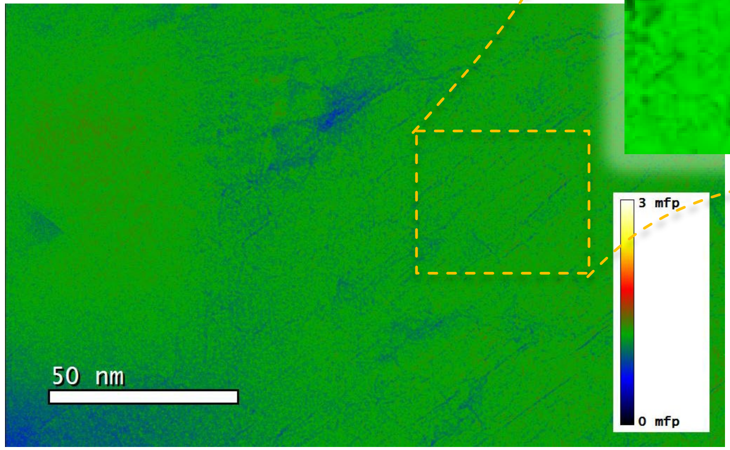
- Banding Reflects randomization during coating the WNCD layer
- Banding corresponds to x3 variation in local W doping
- 2x higher sp^2-C concentration in bright (WC-rich) bands
- Modulation of density and non-thermal x-ray absorption
- Effect on thickness distribution measurement by optical reflection spectroscopy is currently investigated

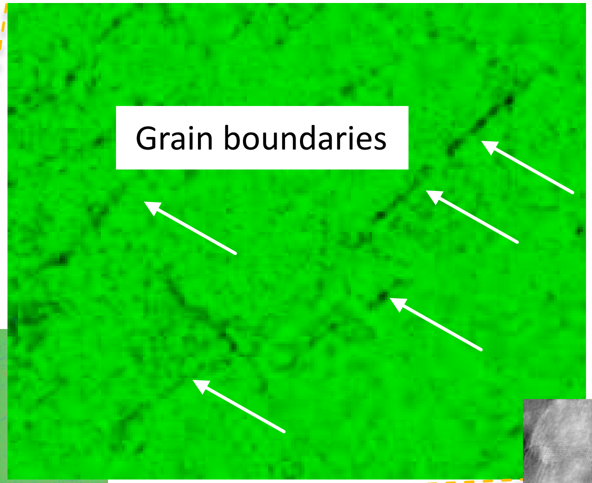
Grain boundaries associated with lower density

zero-loss filtered TEM image

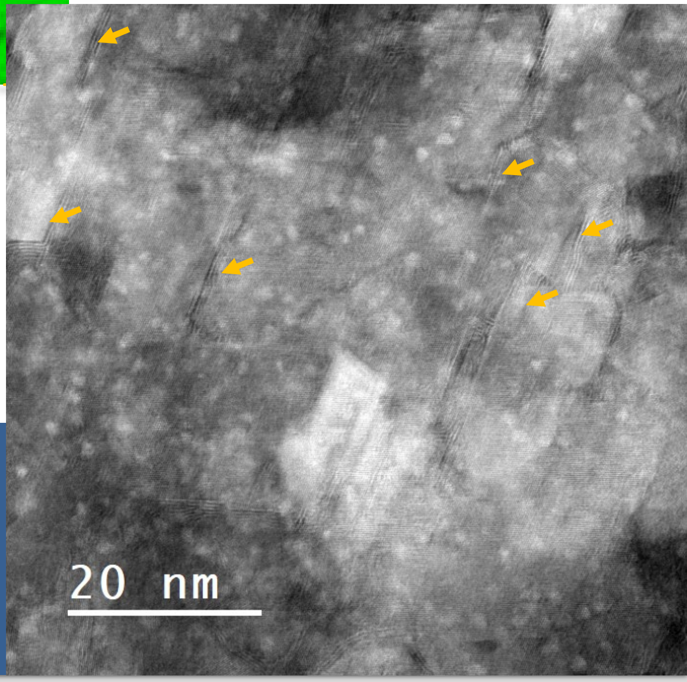


Mean Free Path relative thickness map





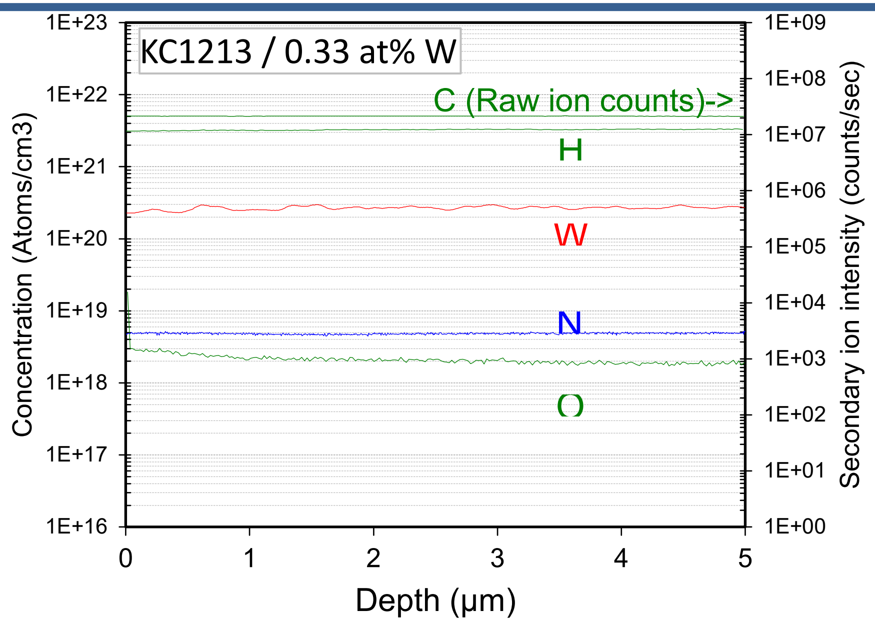
KC 1121
0.4 at.% W/old process

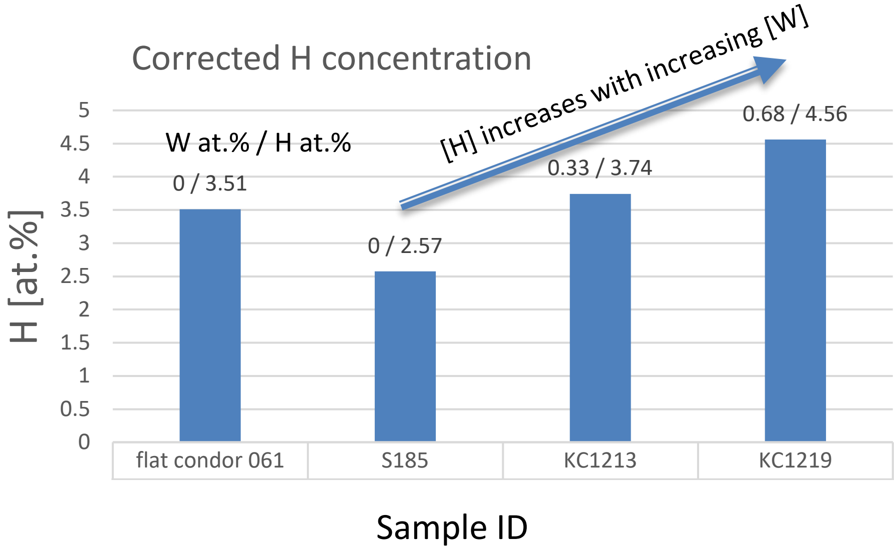


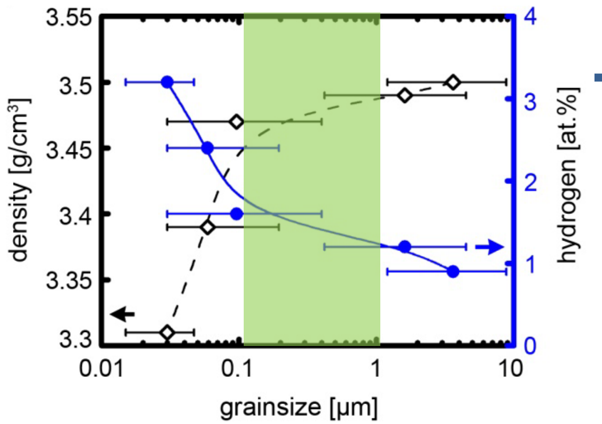
- nano voids and low density material (graphite) between grains
- Line scans reveal grain boundary related density fluctuations of 15%
- TEM confirms the presence of 2-3 graphitic layers at grain boundaries

Hydrogen concentration increases with increasing W concentration

(Secondary Ion Mass Spectroscopy, SIMS)







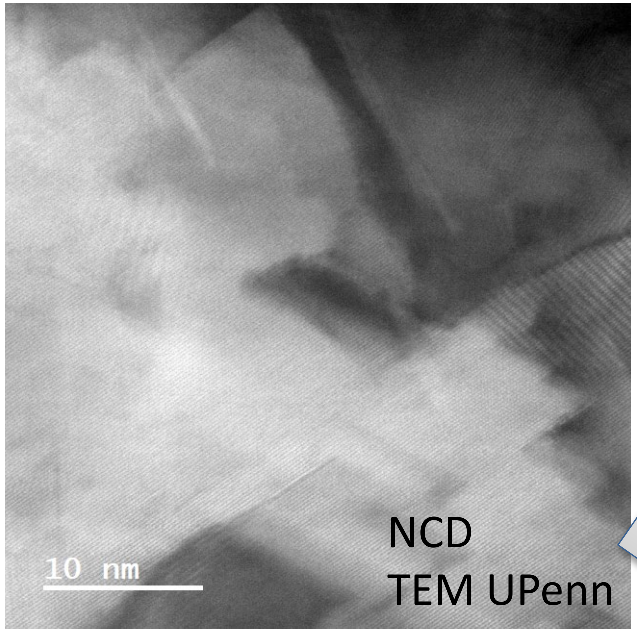
- New process WNCD
- SIMS calibration with Elastic Recoil Detection Analysis (ERDA)

Sample	[W] XRF at.%	[H] SIMS [at.%]	Corrected [H] (x3.5/1.7) [at.%]	N concentration [ppm]
flat condor 061	0	1.71	3.5	204
S185	0	1.25	2.6	56
KC1213	0.33	1.82	3.7	28
KC1219	0.68	2.22	4.6	39

SIMS (Eurofins)

- Hydrogen concentration increases with increasing W concentration (further decreasing density)
- [N] << [H], and [N] of W-NCD (flat) < [N] of NCD (shell)

Characteristic length scales associated with the NCD/WNCD layers range from 0.5 nm to one micron



- Well defined 10-20 nm grains
- Larger regions with similar grain orientation (texture)

0.5 nm Grain boundary layer thickness

2-3 nm WC particles

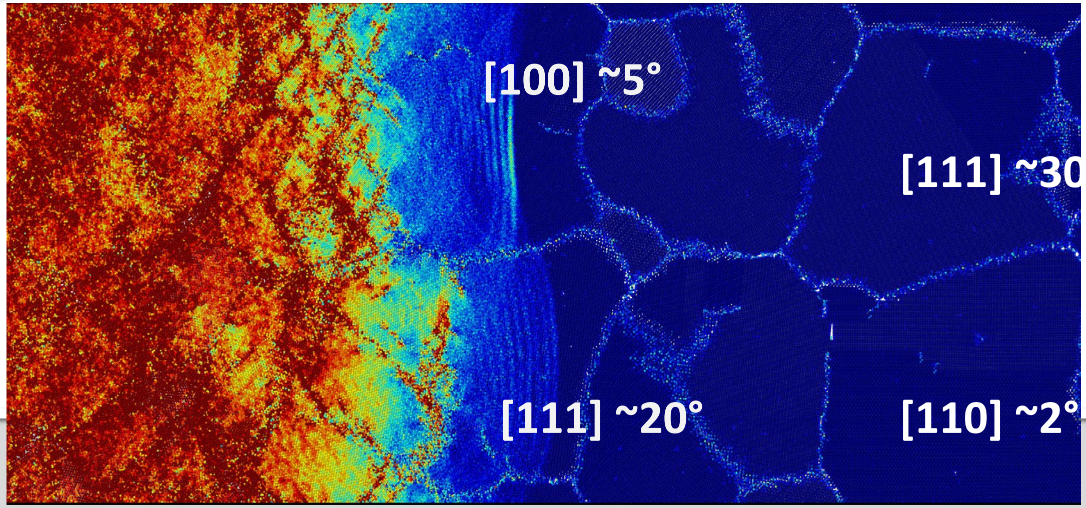
10-100 nm diamond grains

Banding
20-1000 nm radial variation of W-doping level

100-1000 nm texture

Input for MD shock simulation

Academic Collaboration Team project with Prof. Ivan Oleynik (University of South Florida)



37 nm

U_{piston} – 7.6 km/s

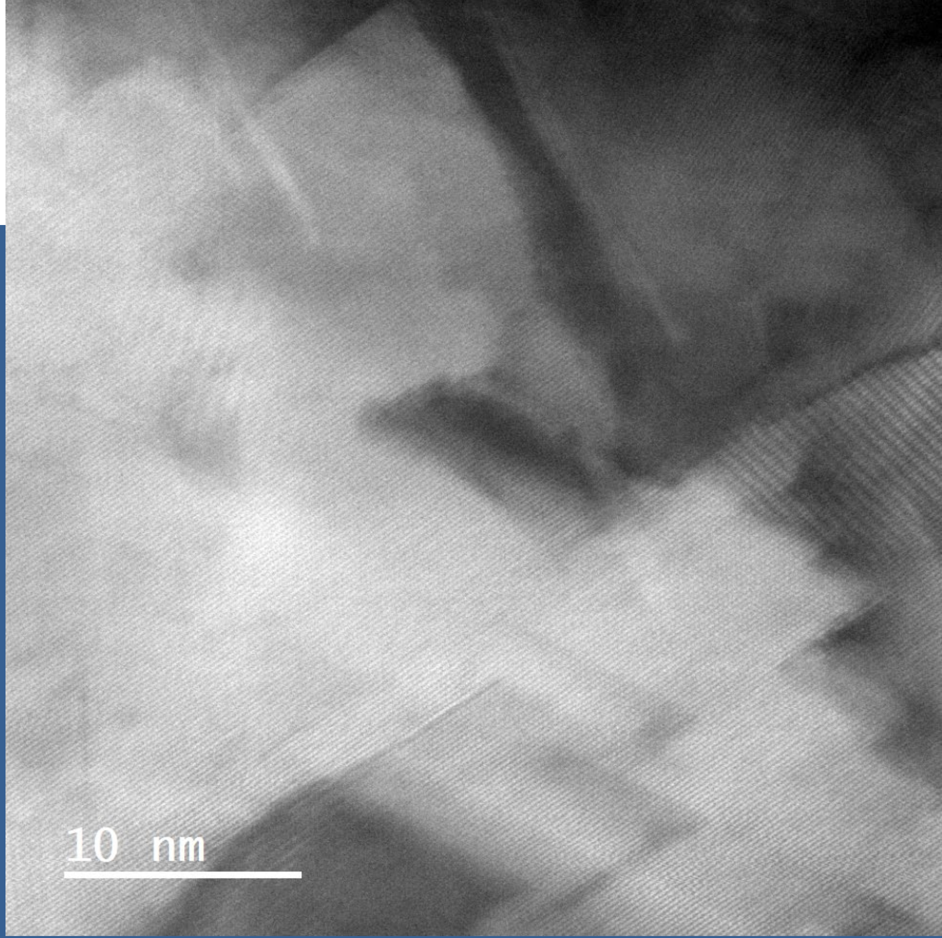
Potential Energy (eV/atom)
-9 -6

5,500 K

5 Mbar pressure

For reference:
Piston speed of 12 km/s causes diamond to fully exit to the liquid region around 10-11 Mbar and 7,500 K.

Summary NCD/WNCD grain structure



- Well defined 10-20 nm grains, smaller in WNCD
- Elongated grains with weak 110 texture in grow direction,
- Grain boundaries have a lower density
  - low angle grain boundaries
  - [H] ~2.5 at.% in NCD *vs* 3.7-4.6 at.% in WNCD
  - [sp^2-C] in NCD < [sp^2-C] in WNCD; increases with increasing [W]
- ~25% of the incorporated W is in the form of small 1-3 nm WC particles embedded in the diamond matrix
- WC lattice fringe spacing ~ 2.4 Å consistent with cubic WC
- Banding reflects radial variation of WC particle density (x3 variation in local W doping)
- Old production batches seem to have a significantly higher sp^2/sp^3 ratio
  Consistent with observation of sp^2–C fringes and lower resistivity/IR transparency

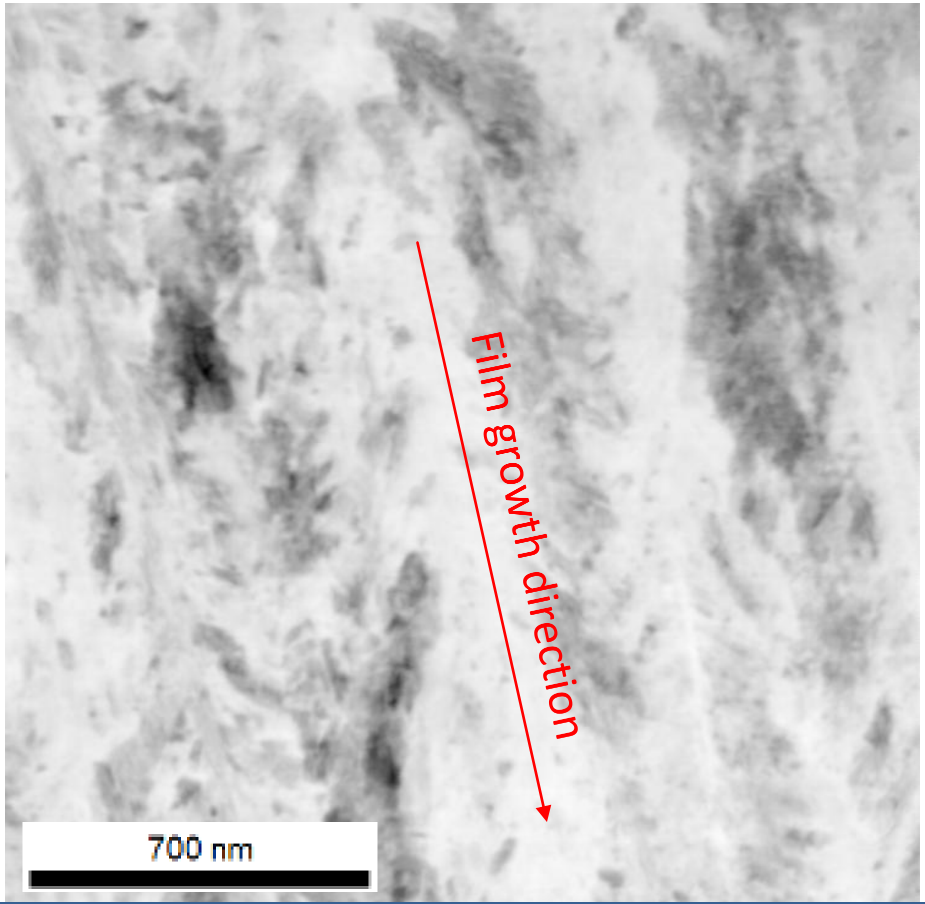
Supplementary Information

Lawrence Livermore National Laboratory

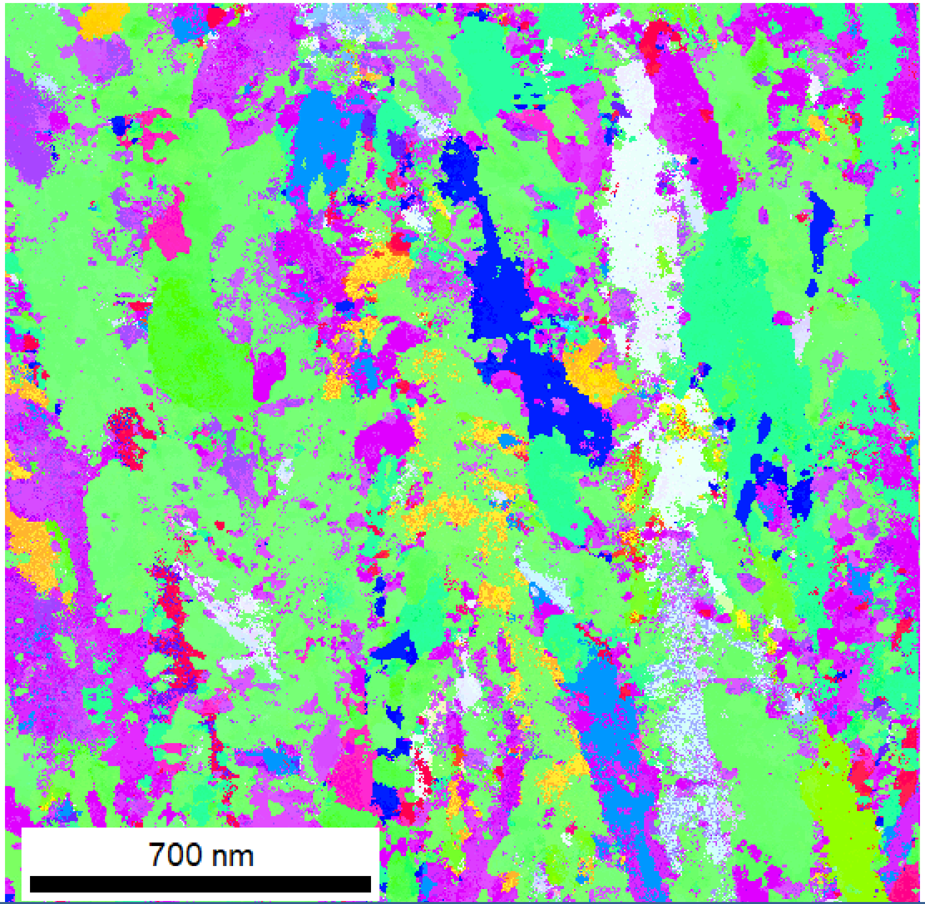
This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

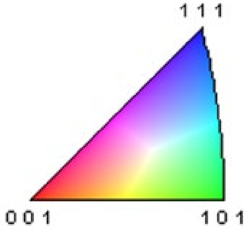
Grain structure KC789 / undoped layer
Parallel to growth direction

Virtual bright-field image (diffraction contrast)



Grain orientation map



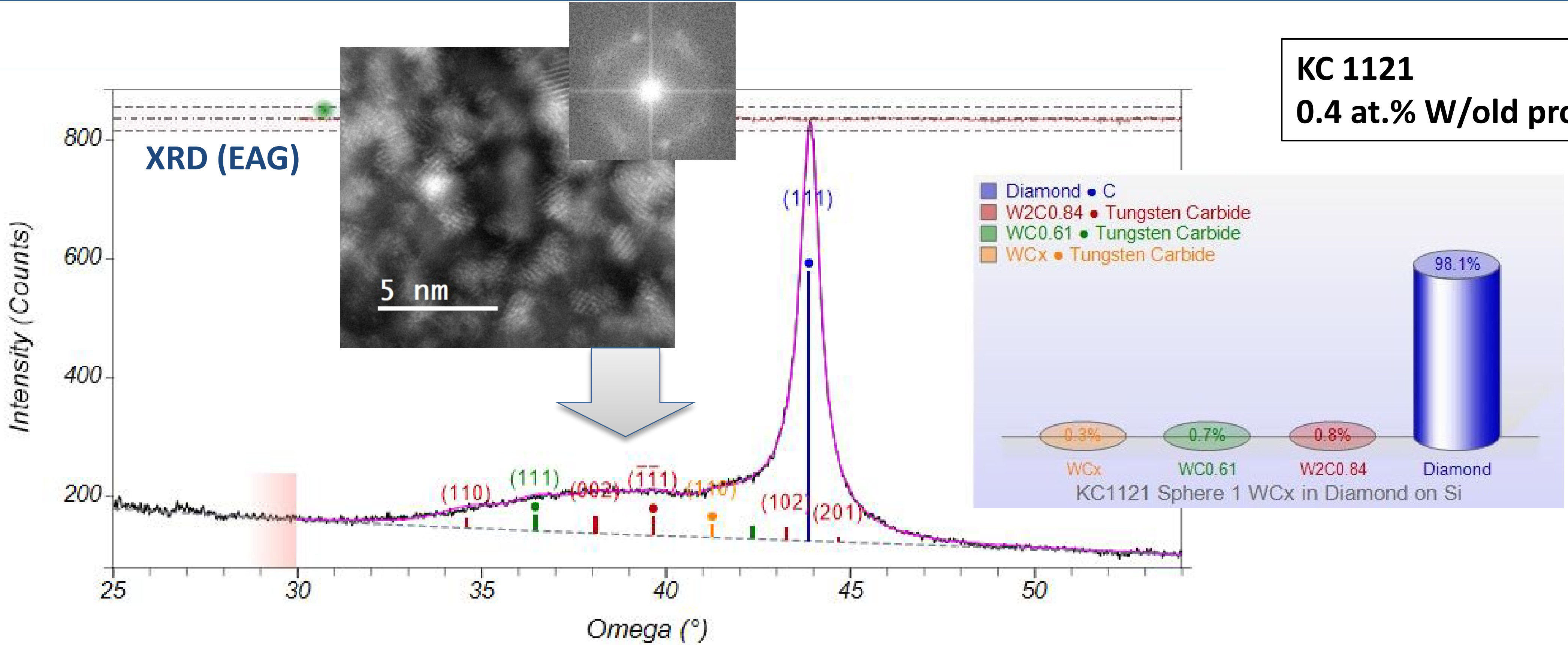


TEM grain orientation map
Swanee Shin / LLNL

Elongated, several hundred nm long regions with similar grain orientation

Tungsten carbide: phase identification

KC 1121
0.4 at.% W/old process

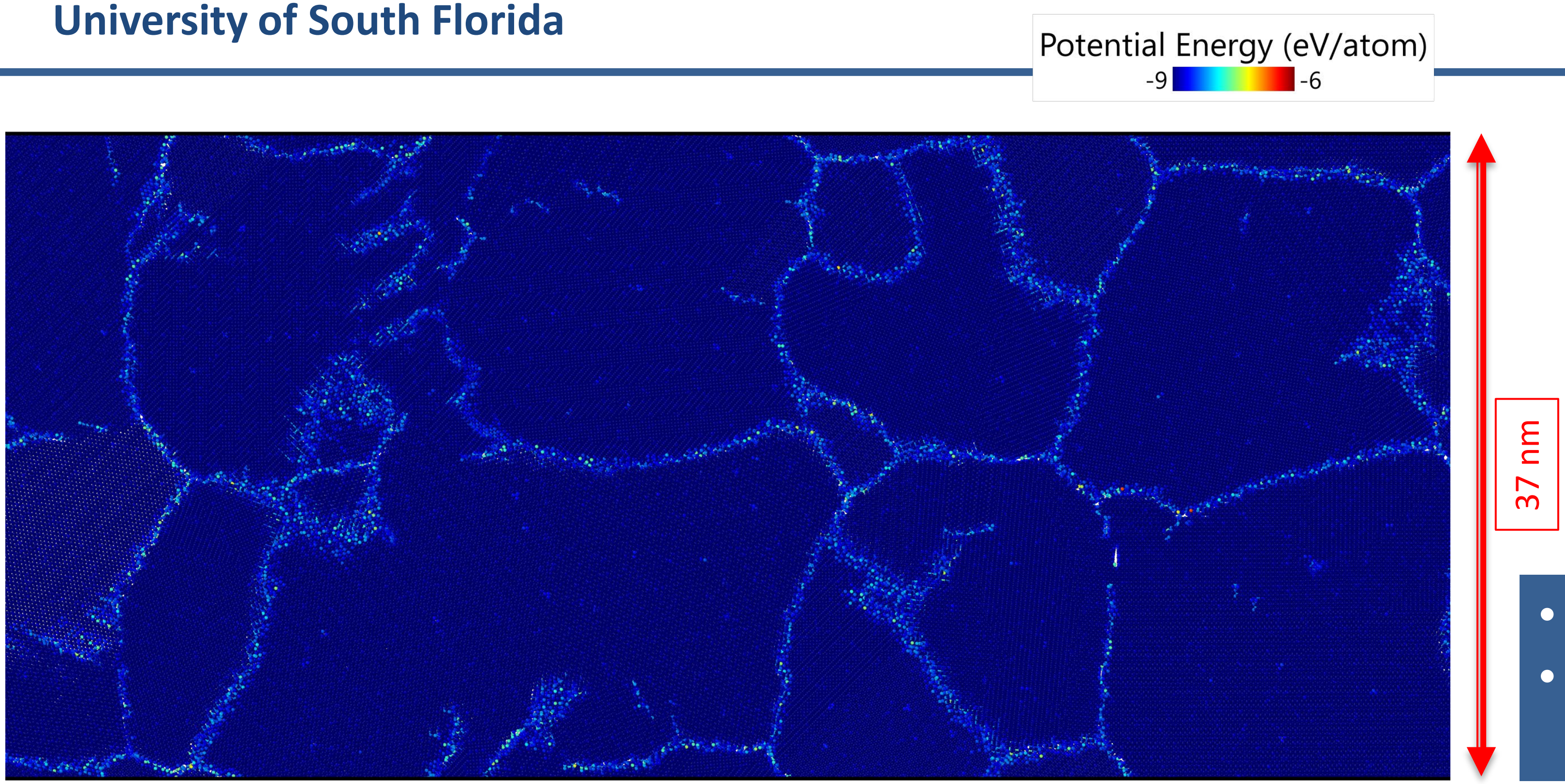


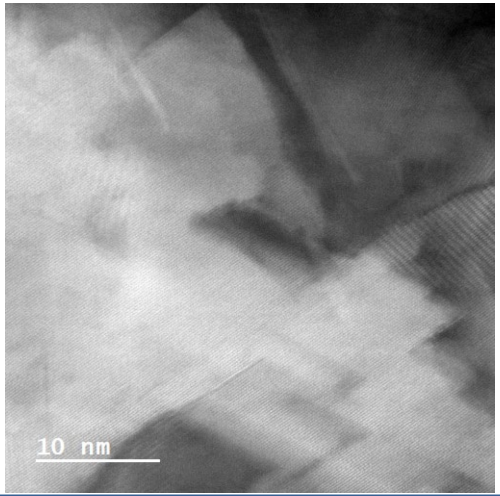
Whole Pattern Fitting (WPF) was used to attempt to quantify the W carbide phases with respect to the diamond

Presence of multiple (disordered) WC phases necessary to explain the broad WC XRD peak

Construction of realistic unshocked NCD MD samples

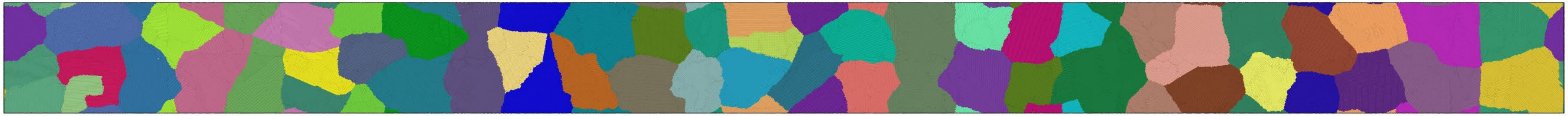
Academic Collaboration Team (ACT) collaboration with Prof. Ivan Oleynik / Dr. Joe Gonzalez from the University of South Florida





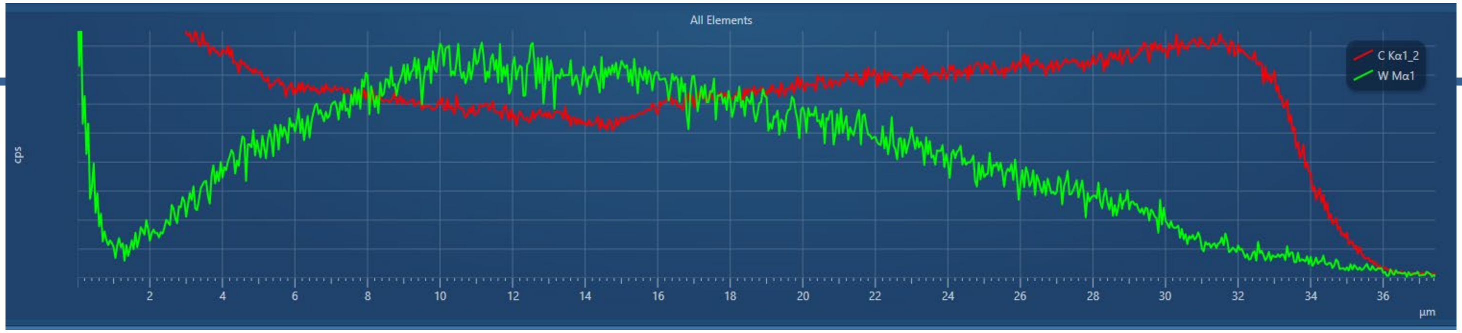
NCD
TEM UPenn

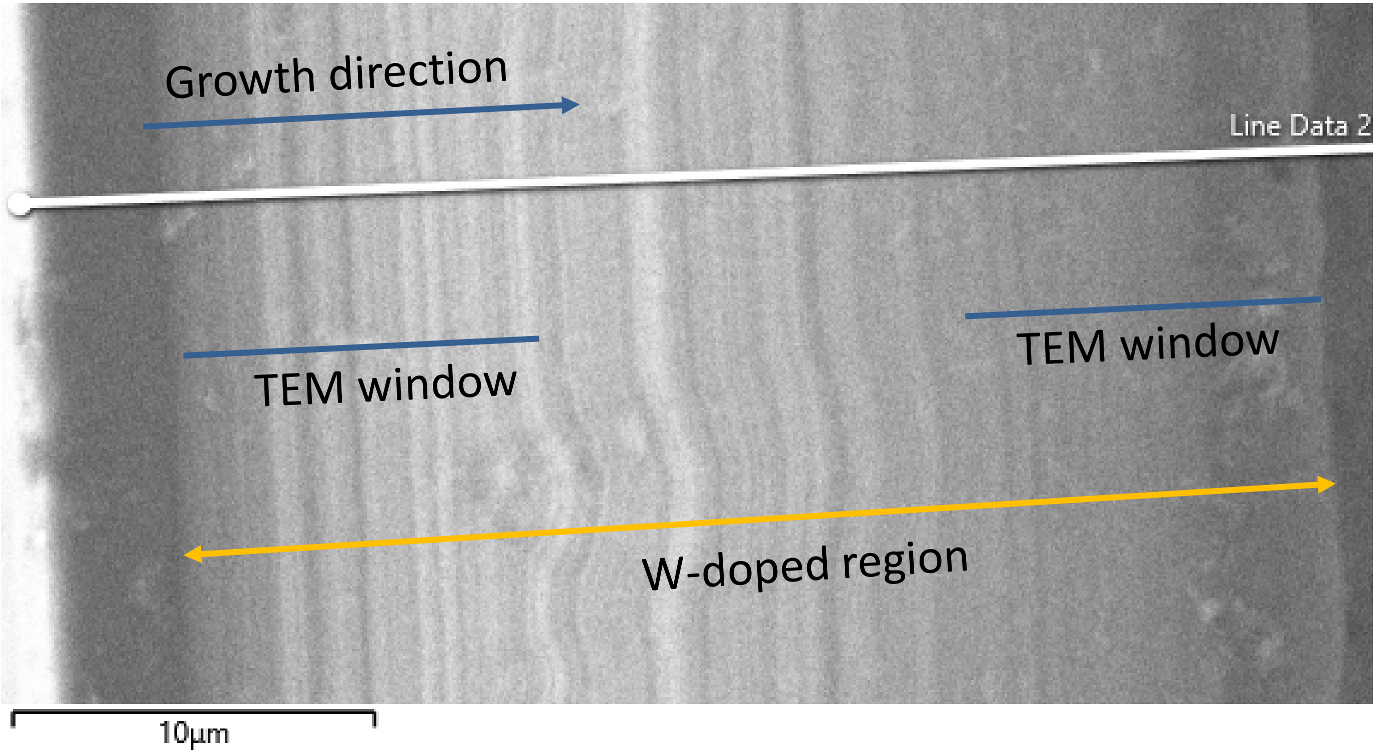
- Well defined 10-20 nm grains
- Larger regions with similar grain orientation (texture)



200 million atoms, after the nucleation/decompression protocol
Average grain size ~ 15 nm diameter

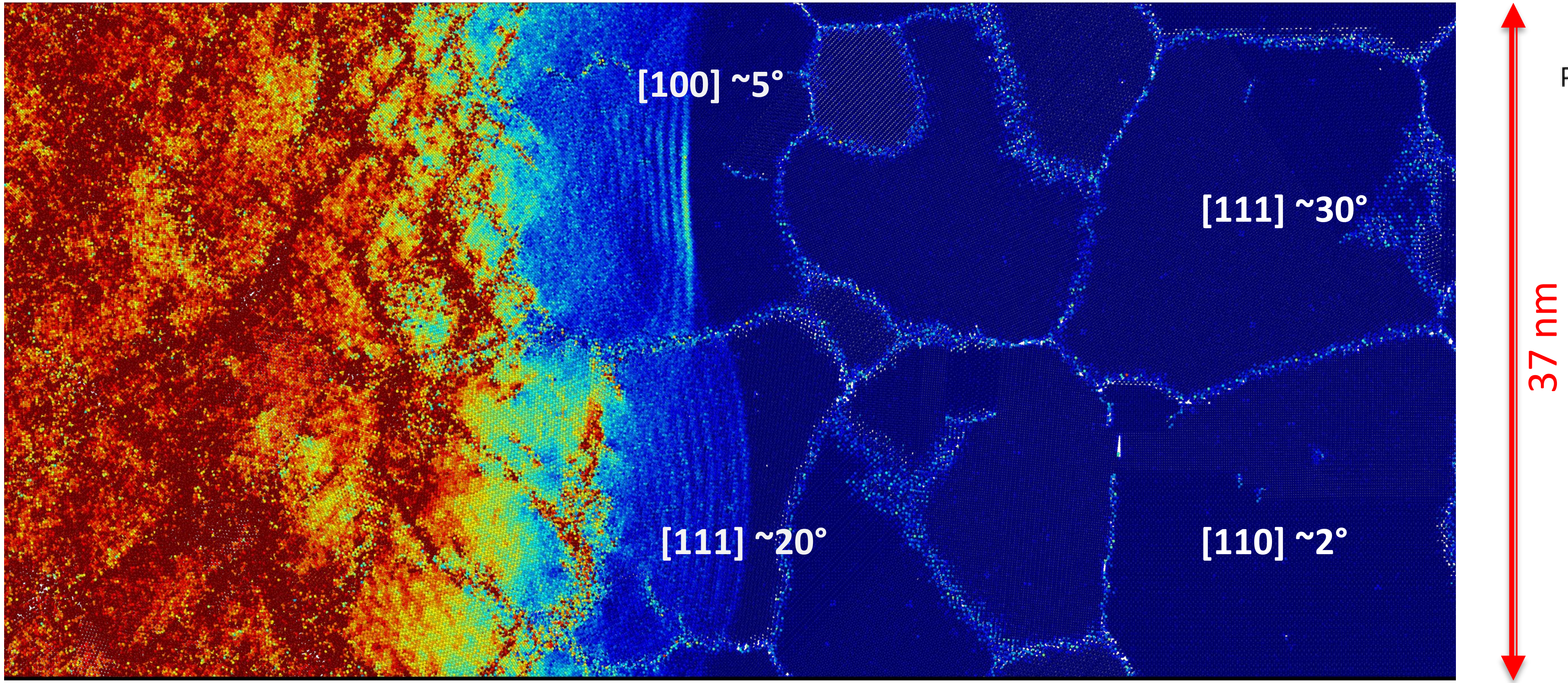
KC1317 doping gradient / cross-sectional SEM/EDS





Characterization data enable realistic NCD MD models to study the shock response

Academic Collaboration Team (ACT) collaboration with Prof. Ivan Oleynik / Dr. Joe Gonzalez from the University of South Florida



U_{piston} – 7.6 km/s

Potential Energy (eV/atom)

-9 -6

5,500 K

5 Mbar pressure

For reference:
Piston speed of 12 km/s causes diamond to fully exit to the liquid region around 10-11 MBar and 7,500 K.

Ripple in the shock front imprinted by grain orientation

Grain boundary volume

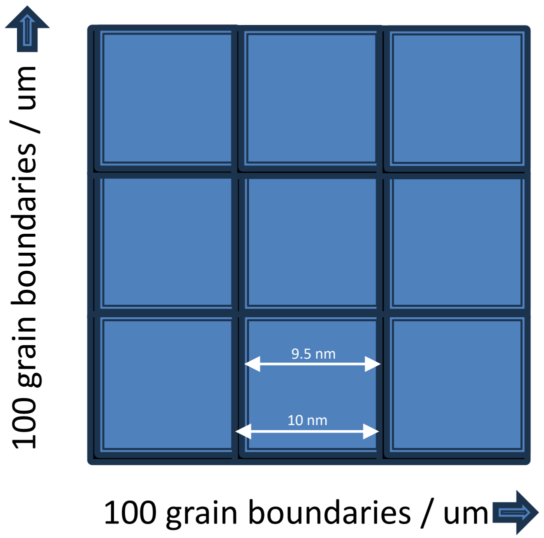
Assumptions:
1) Core of each grain has full single crystal diamond density of 3.5 g/cc
2) Grain boundary is associated with graphite with a local density of 2.2 g/cc

Data:
1) Measured density of NCD is 3.3 g/cc
2) Grain size distribution shows a peak at around 10 nm (TEM images and OIM software)

Conclusions:

1) Explaining the measured NCD density of 3.3 g/cc requires that the graphitic grain boundary layer occupies ~10% of the volume: 0.88 x 3.5 g/cc + 0.12 x 2.2 g/cc = 3.34 g/cc

2) With a total grain boundary length of 200 um^{-1} the thickness of the grain boundary layer needs to be 0.5 nm to explain the measured density of 3.3 g/cc



Area per 10 nm grain: $A_{10\ nm} = 100\ nm^2$

Area grain boundary: $A_G = 2 \times 10 \times 0.5\ nm^2 = 10\ nm^2$

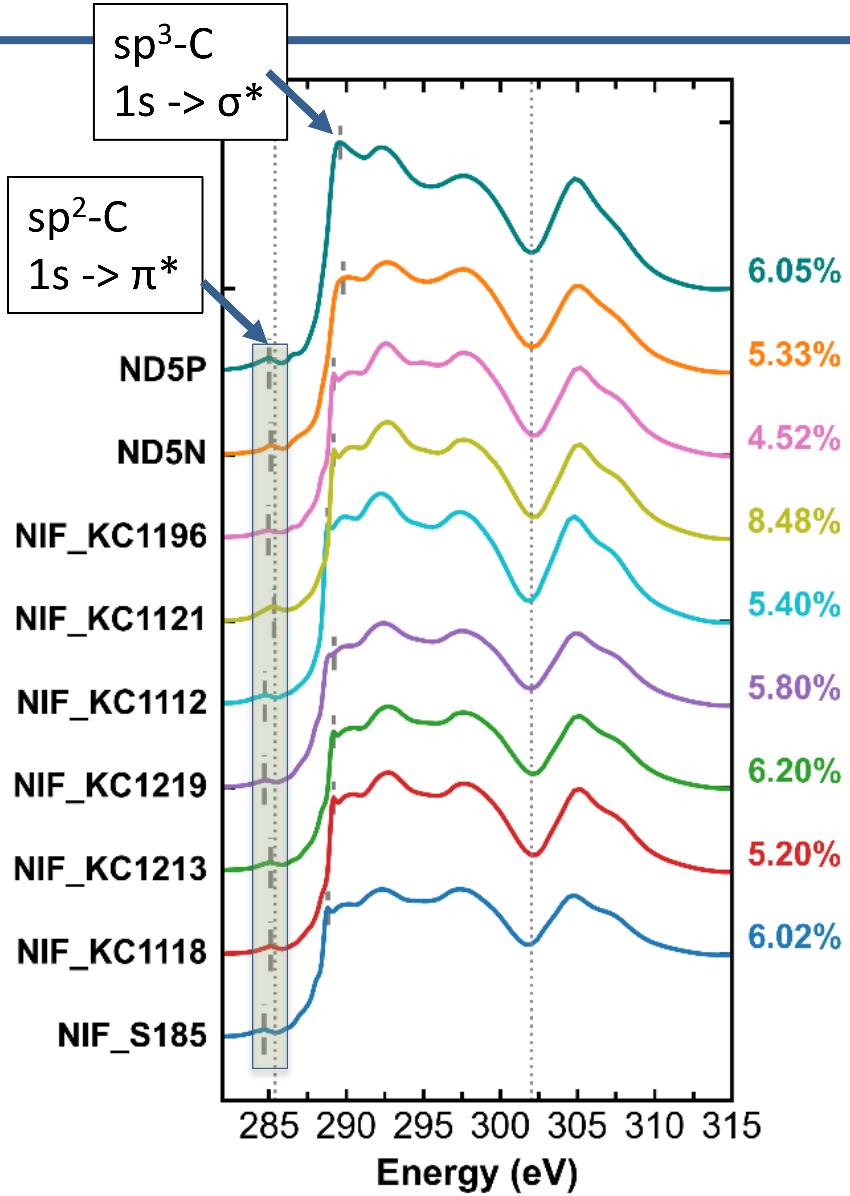
Area core of a grain: $A_C = 9.5 \times 9.5\ nm^2 = 90.25\ nm^2$

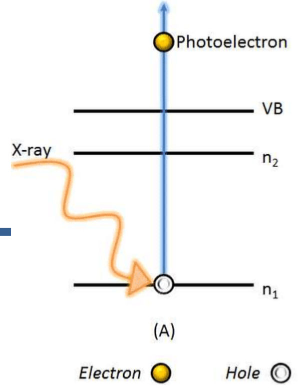
$A_G/A_{10\ nm} = 0.1$

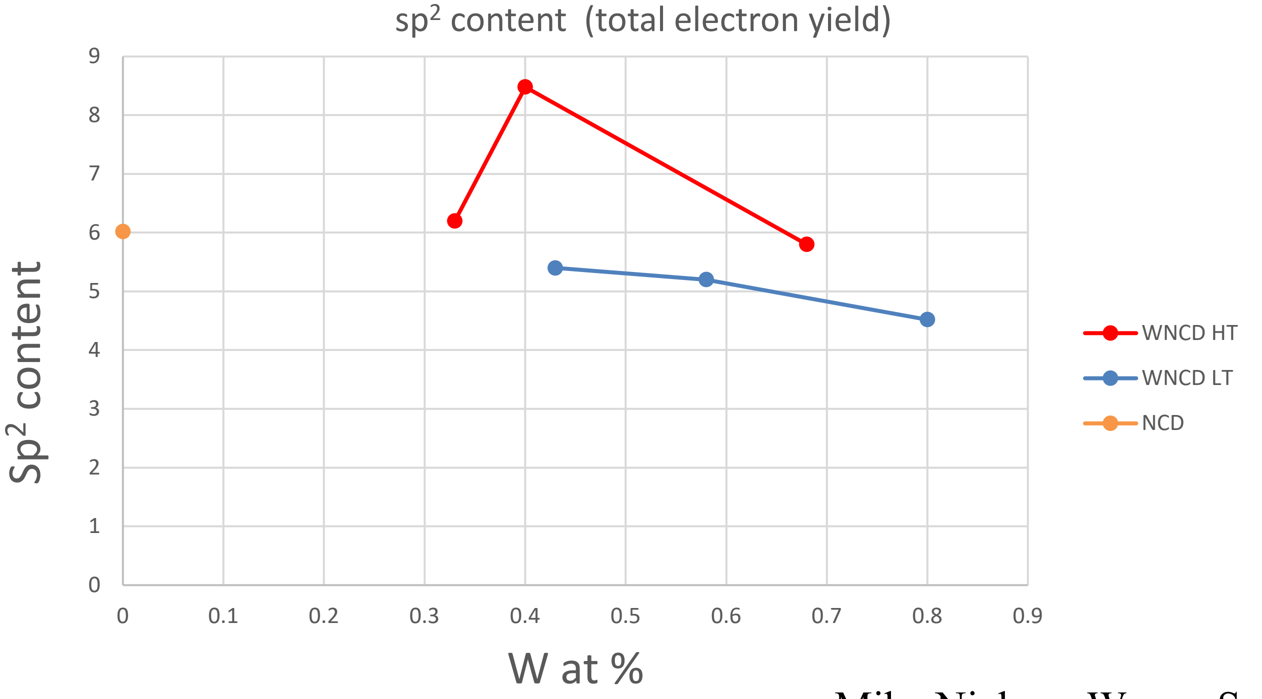
Total grain boundary length per um^2 = 100 x 1 um + 100 x 1 um = 200 um^{-1}

Graphitic carbon (C-sp2) content:

Volumetric measurement by Near Edge X-Ray Absorption (NEXAFS)



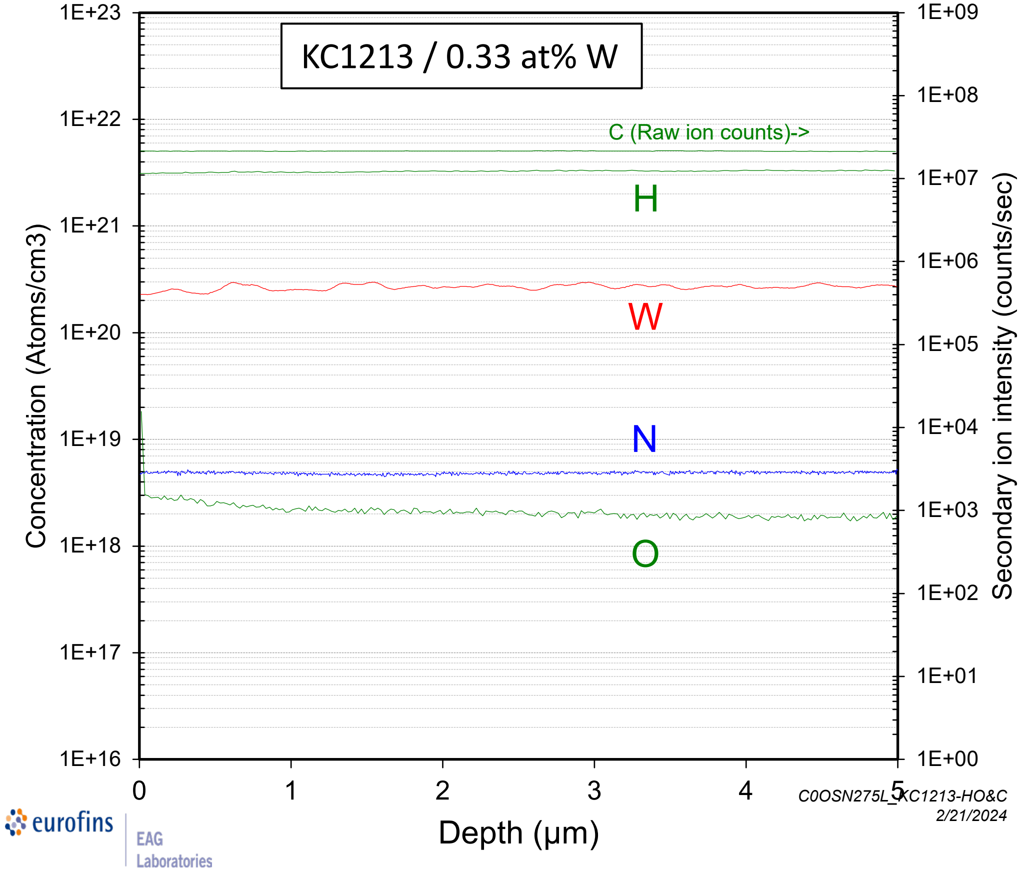


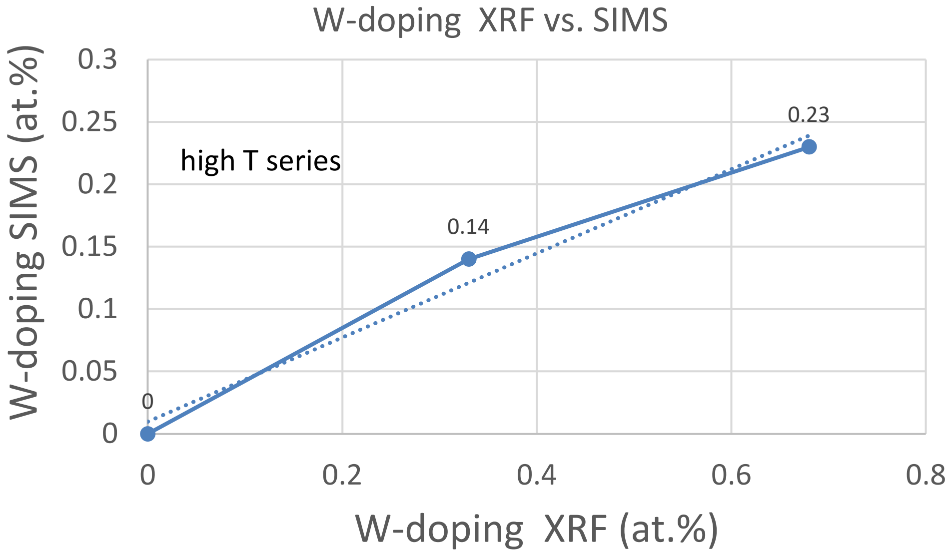


Mike Nielsen, Wenyu Sun (LLNL)

- [sp^2-C] high T > [sp^2-C] low T
- But [sp^2-C] does not seem to increase with [W] ?

W content:
Secondary Ion Mass Spectroscopy (SIMS)





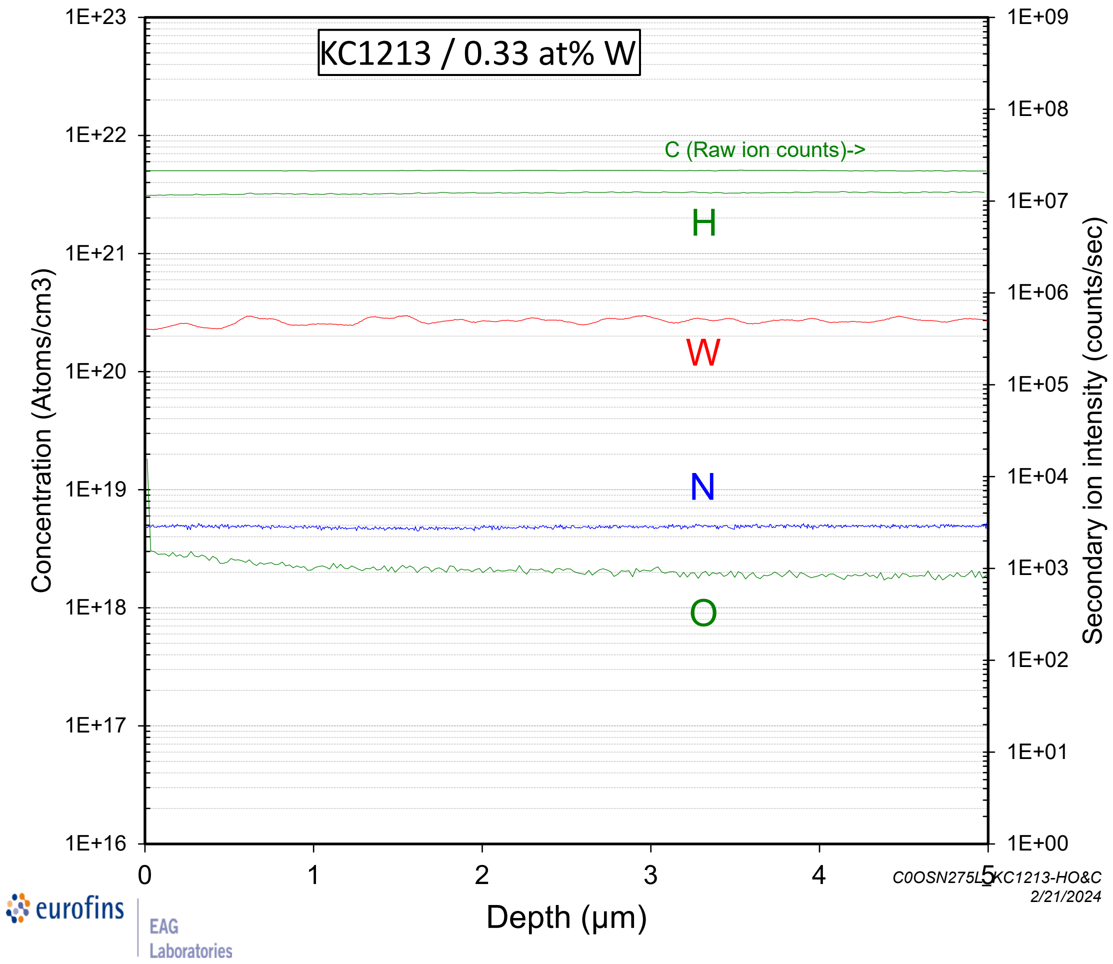
SIMS (Eurofins)

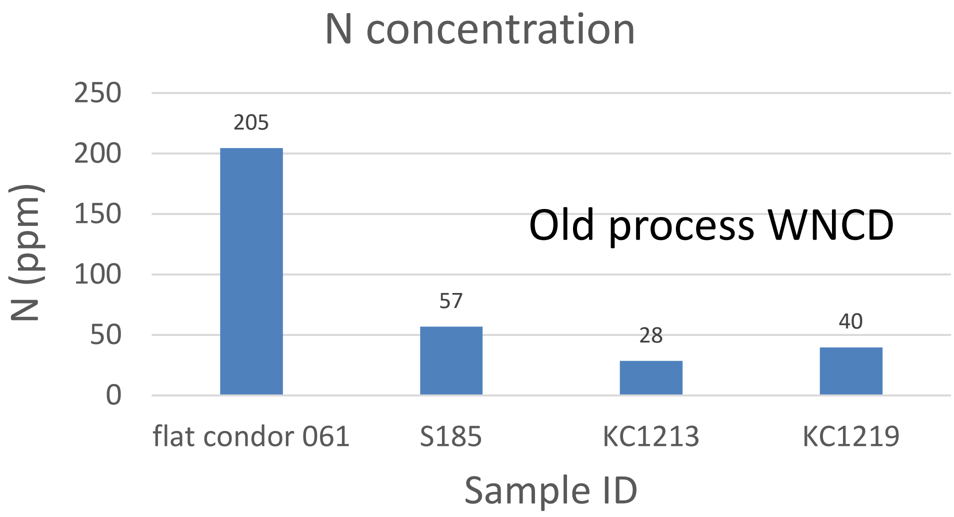
sample	W doping XRF at%	W doping SIMS at.%	type
S185	0	0	low T
KC1213	0.33	0.14	high T
KC1219	0.68	0.23	High T

Good correlation [W] SIMS and XRF, but [W] SIMS factor 3 too small

Nitrogen content:
Secondary Ion Mass Spectroscopy (SIMS)

SIMS (Eurofins)





Sample	[W] XRF at.%	[N] (atoms/cc)	[N] (ppm)
flat condor 061	0	3.6E+19	204
S185	0	1E+19	56
KC1213	0.33	5E+18	28
KC1219	0.68	7E+18	39

- [N] << [H], and [N] of W-NCD (flat) < [N] of NCD (shell)
- Shells and flats differ a lot!