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Towards Single Grain Bi_2Te_3 Nanowires: Thermal Annealing Investigated using a Combined STEM/CBED Mapping Technique

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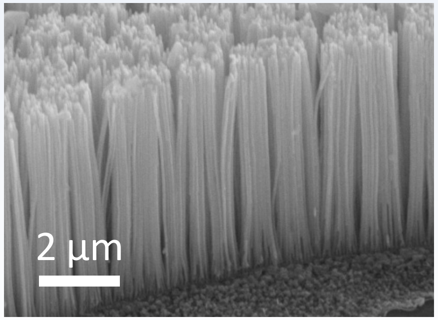
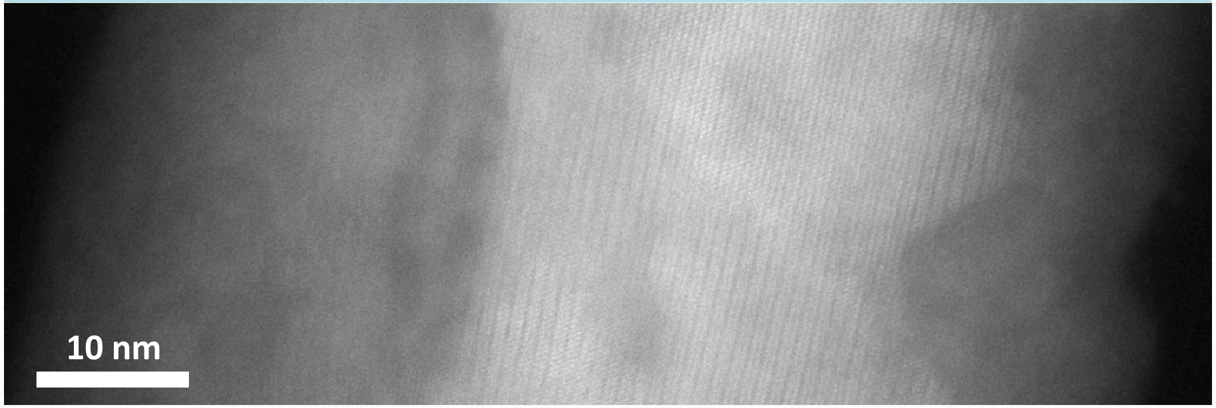
Crystallinity of TE NWs Improves with Thermal Annealing

Bi_2Te_3 NWs, Pulsed-Current Deposited into AAO Templates
75 nm diameter, ~ 6 µm in length Limmer, et al., *J. Elec. Soc.*, **2012**

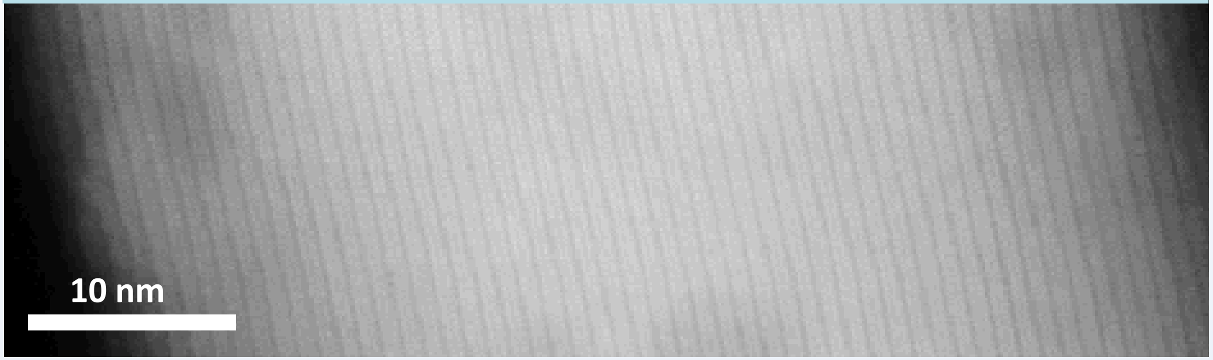


Initially crystallinity is relatively poor, but can improve with annealing.
Changes will have dramatic affect on ZT!

200 °C, 30 min Anneal, HAADF STEM Micrograph



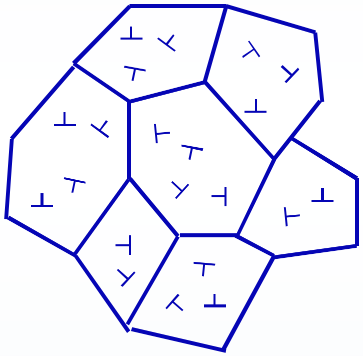
300 °C, 30 min Anneal, HAADF STEM Micrograph



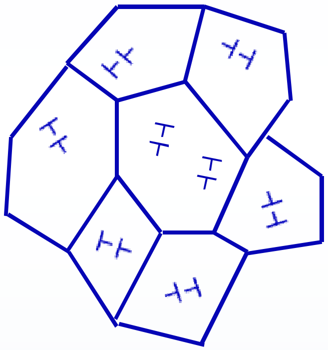
How to quantify changes in crystallinity microscopically during the annealing process?

Changes in Crystallinity During Thermal Annealing

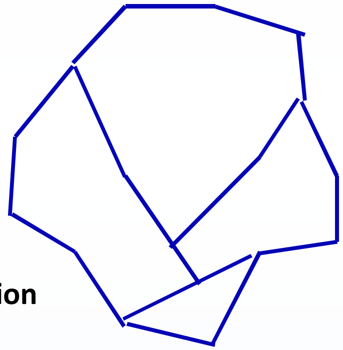
What do we expect to occur during the annealing of our NW's?
Bulk Analog: Two stages during annealing of bulk deformed materials.



Recovery



Recrystallization



Defect migration:
- climb, slip leading to polygonization and annihilation

Vacancy/point defect migration

Grain "nucleation"

Grain boundary migration

Grain growth: including ripening, sub-grain coalescence

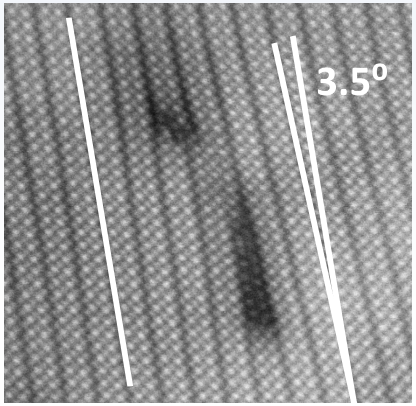
To assess any enhancement in crystallinity for our NW's, we want a microscopic technique which is sensitive to both stages of annealing.

Outline

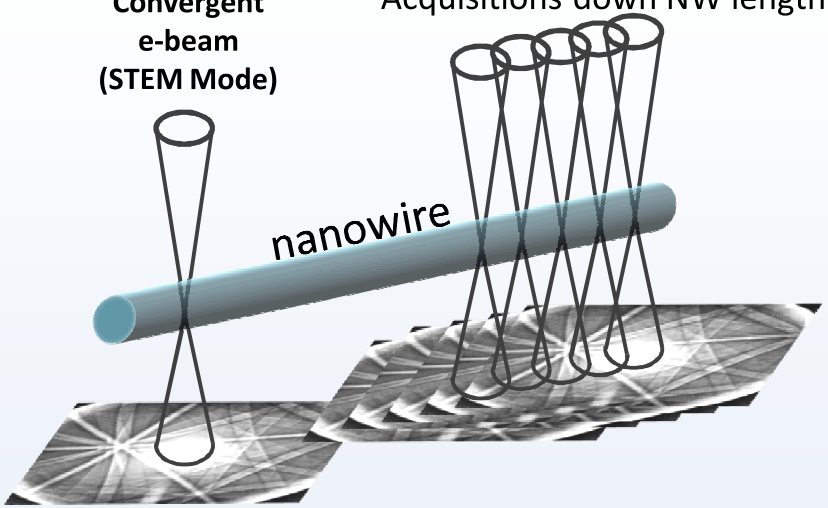
1. Description of Technique
2. Experimental Overview
3. In-Situ Annealing: Recovery Stage Analysis
4. Ex-Situ Annealing: Recovery Stage Analysis
5. Ex-Situ Annealing: Recrystallization Stage Analysis
6. Conclusions

Our Approach: STEM/CBED Mapping

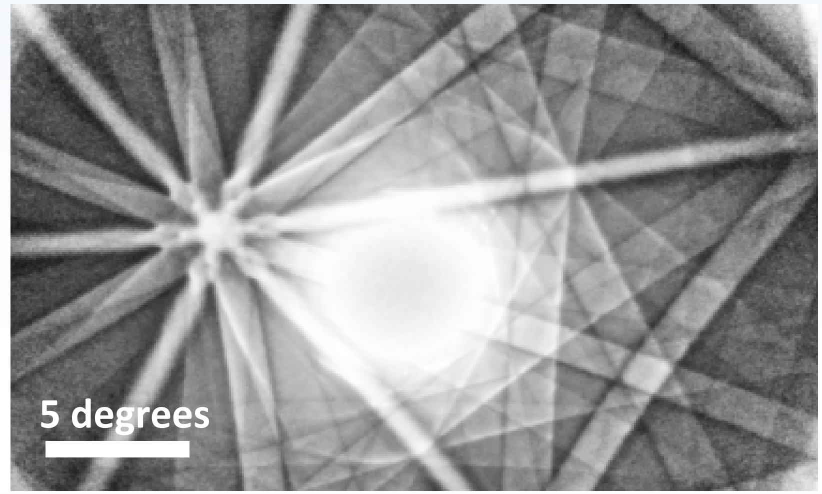
Series of Dislocations → Crystal Zone Axis Tilt



Acquisition for a Nanowire



Kikuchi Lines & Kossel Patterns



Details

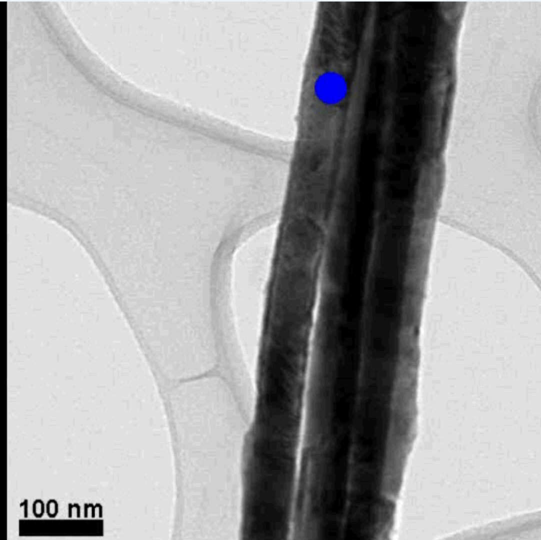
Spatial Resolution: 1 nm

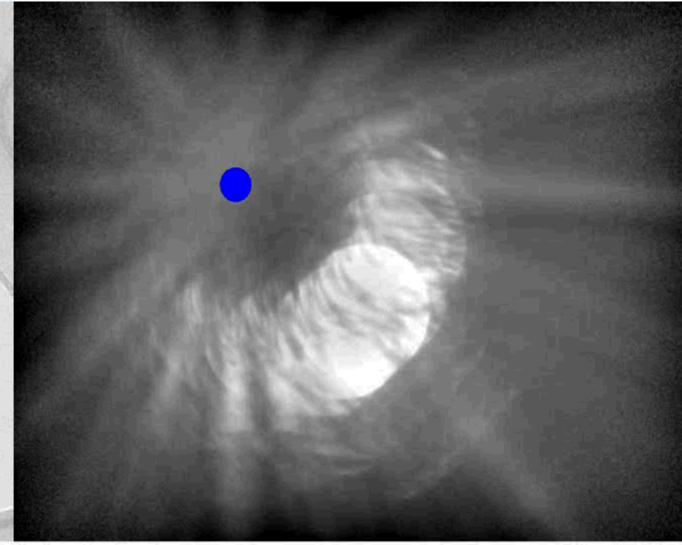
Angular Resolution: ~0.03 °

Considering 2 tilt axes

ΔΘ/Δx corresponds to dislocation induced crystalline disorder

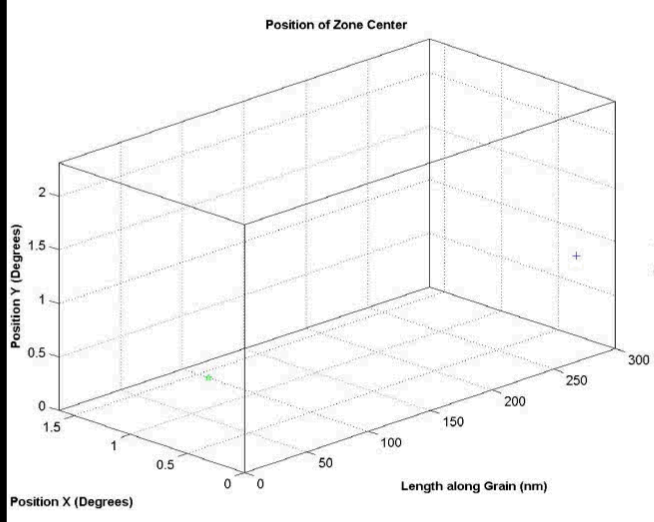
Beam Position During CBED Acquisition (Δx= 3 nm)

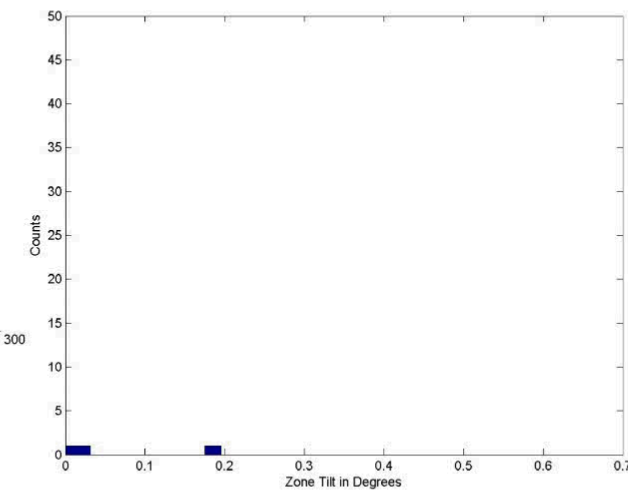




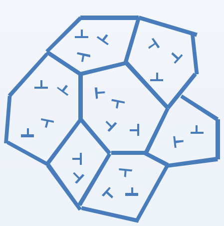
Following the [-10 -5 1] zone

Position of Zone Center plotted down the length of the grain



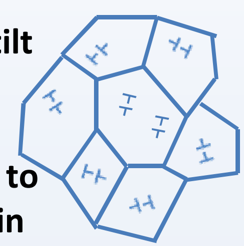


Histogram of the amount of Zone tilt between acquisitions (ΔΘ/Δx)



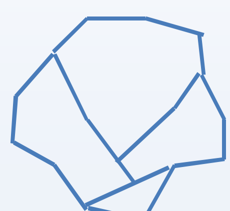
Intragrain defects: zone tilt changes

Corresponding to progress within recovery phase



Large angle grain boundaries: Shift on Kikuchi Map

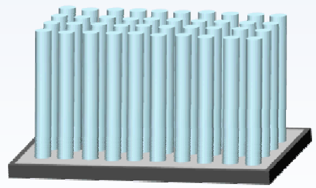
Corresponding to progress within recrystallization phase



Assessment of progress within both stages of annealing at high angular and spatial resolution!

Two Experimental Approaches

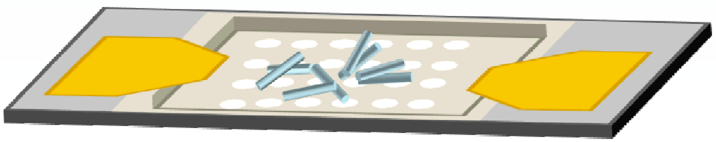
Free-standing Bi_2Te_3 NW's



In Situ Heating Experiment

Same Positions on specific Wires; Annealed in vacuum of TEM

1. Spotted onto TEM Heating Stage Substrate



2+. Acquisition, anneal at elevated temp, repeat acquisition, ect.

Annealing Conditions Analyzed

No anneal

200 °C for 30 min

200 °C for 8 hr

250 °C for 30 min

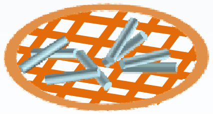
Material lost stoichiometry when taken to 300 °C owing to lost Te

Same positions of same wires analyzed: Direct comparisons between as-deposited and annealed wires!

Ex Situ Heating Experiment

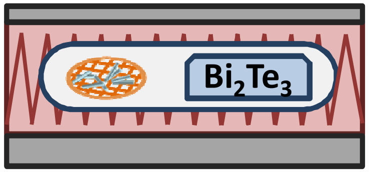
Same wires, annealed with bulk Bi_2Te_3 to maintain stoichiometry

1. Spotted onto TEM Grid



2. Acquisition

3. Sealed in Ampoule with Bulk Bi_2Te_3 and Annealed in Oven



4+. Repeat Acquisition, then anneal, ect.

Annealing Conditions Analyzed

No anneal

150 °C for 45 min

250 °C for 45 min

350 °C for 45 min

Material maintained stoichiometry to 350 °C

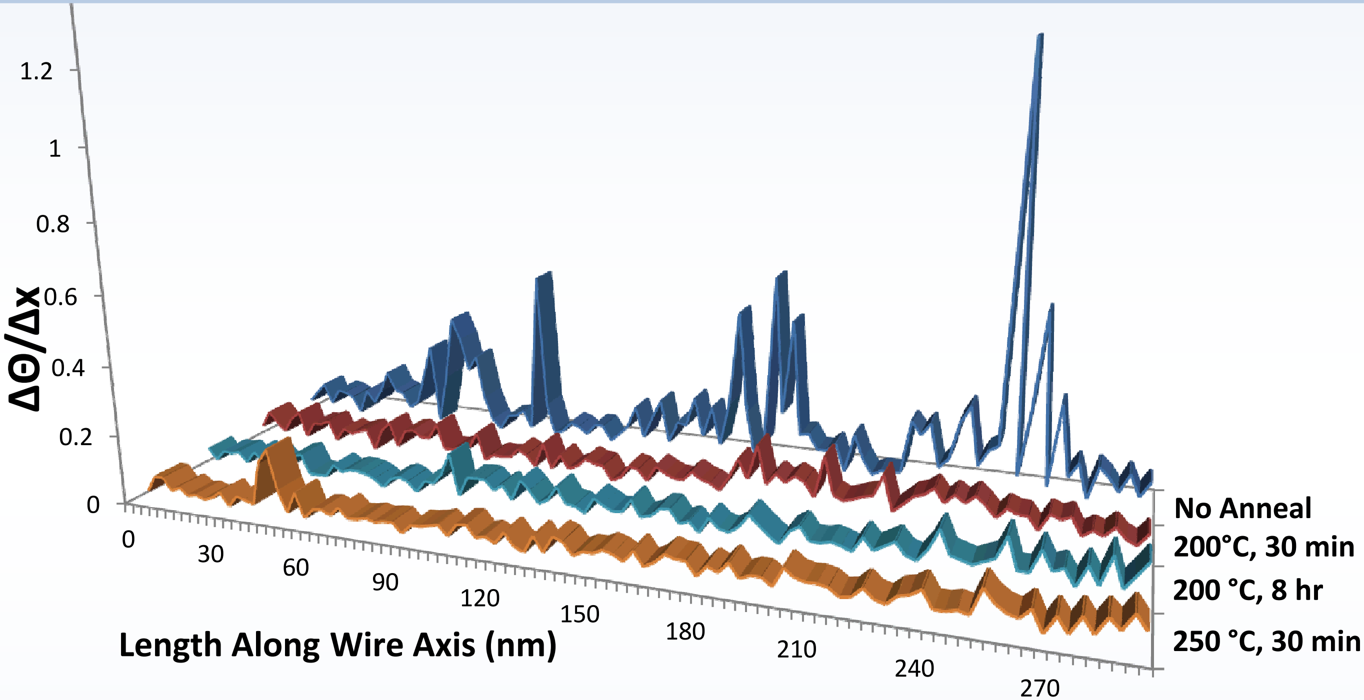
In Situ Annealing – Intragrain Crystallinity Analysis of a Single Grain

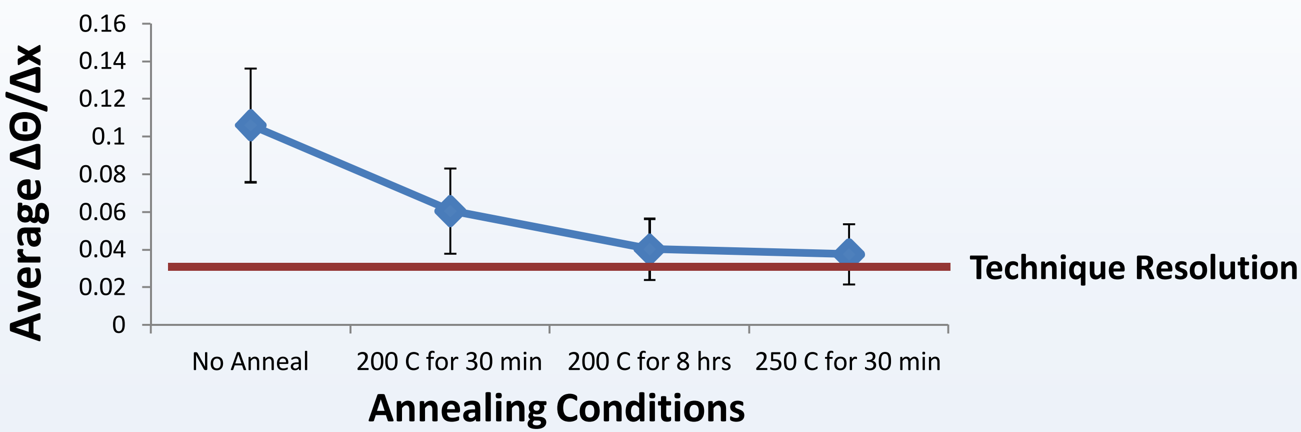
Dislocation Induced Disorder within a Specific Grain as a Function of Annealing

Δx = 3 nm

300 nm length of wire analyzed

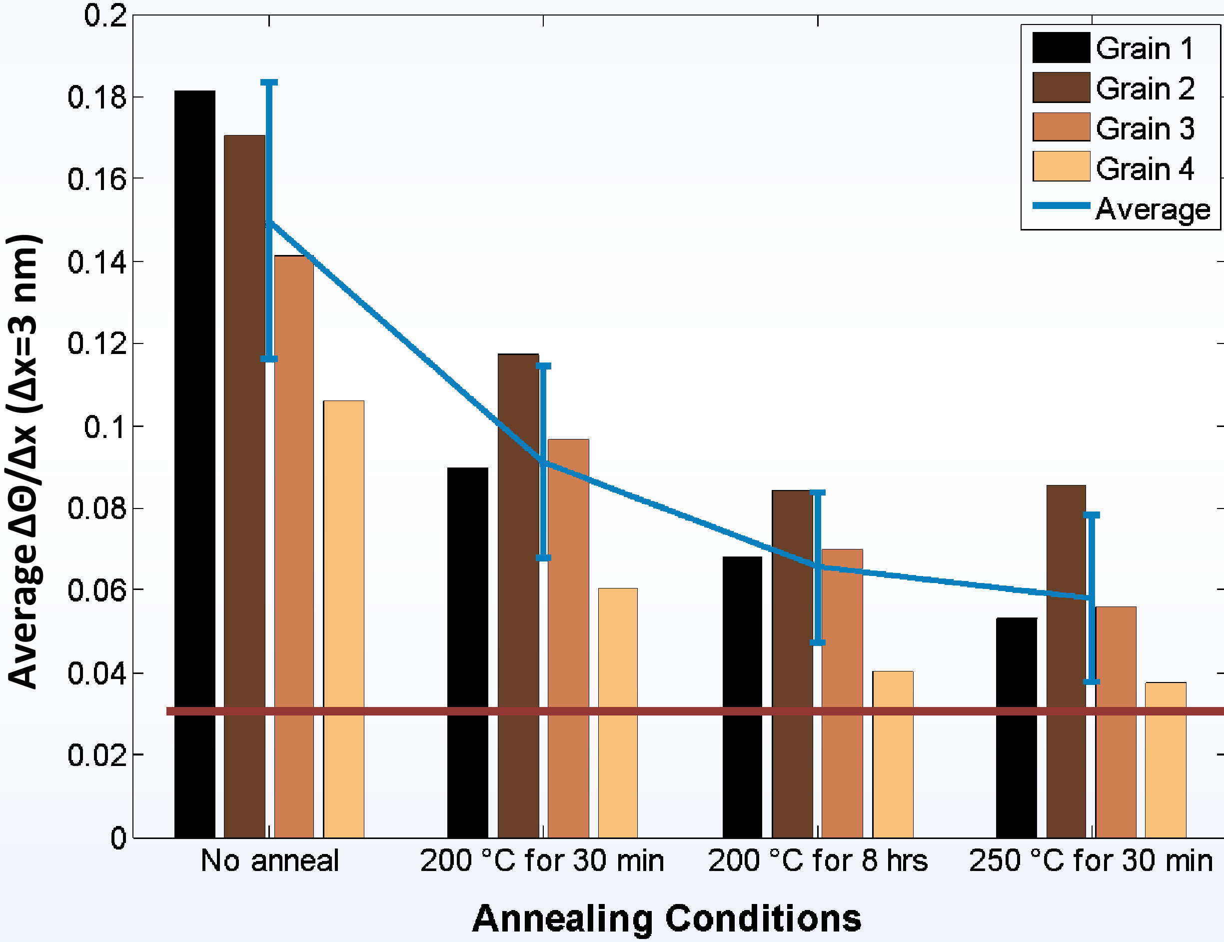
Same wire region analyzed





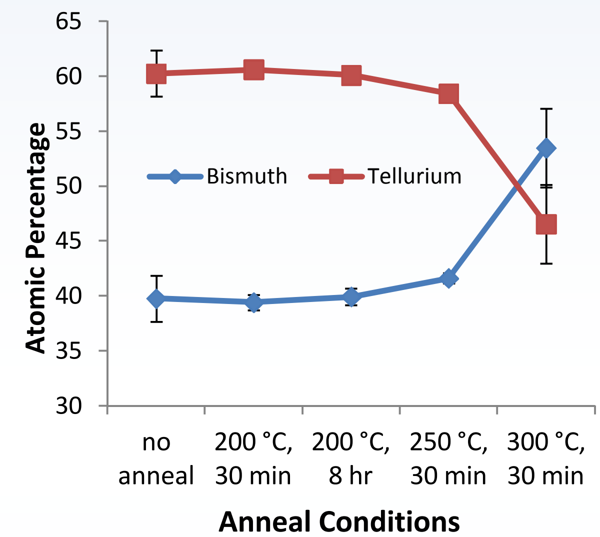
In Situ Annealing – Intragrain Crystallinity Analysis of Multiple Single Grains

Dislocation Induced Disorder for all Grains under Annealing Conditions



Technique Resolution

EDS Data



Significant Te loss at higher T (due to TEM vacuum)

Progress within the recovery phase apparent with a decrease in dislocation induced disorder

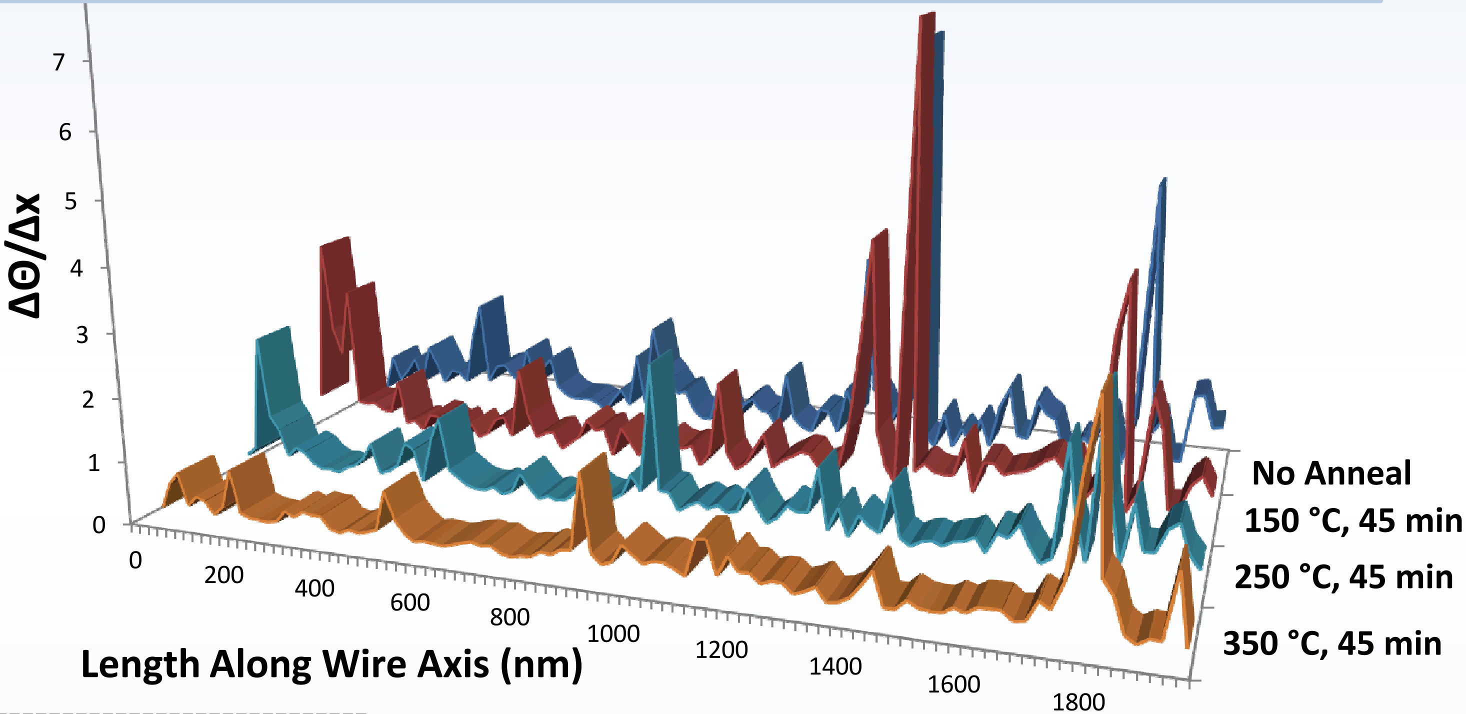
Ex Situ Annealing with Bulk Bi_2Te_3 - Analysis of a Specific Wire

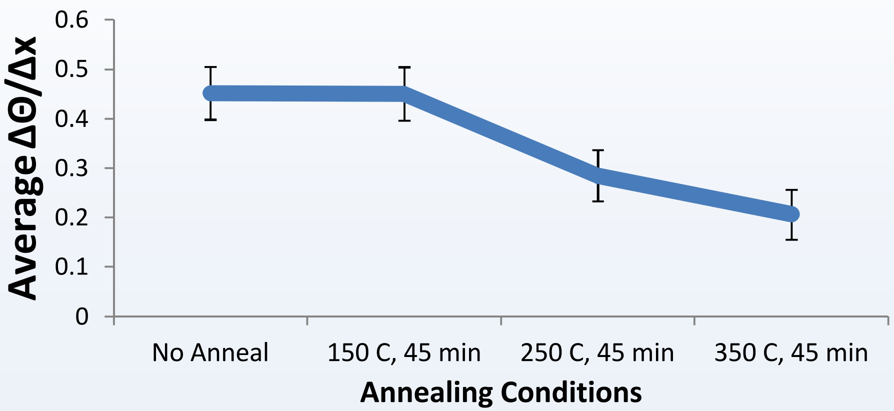
Dislocation Induced Disorder within a Specific Wire as a Function of Annealing

Δx = 20 nm

2 µm length of wire analyzed

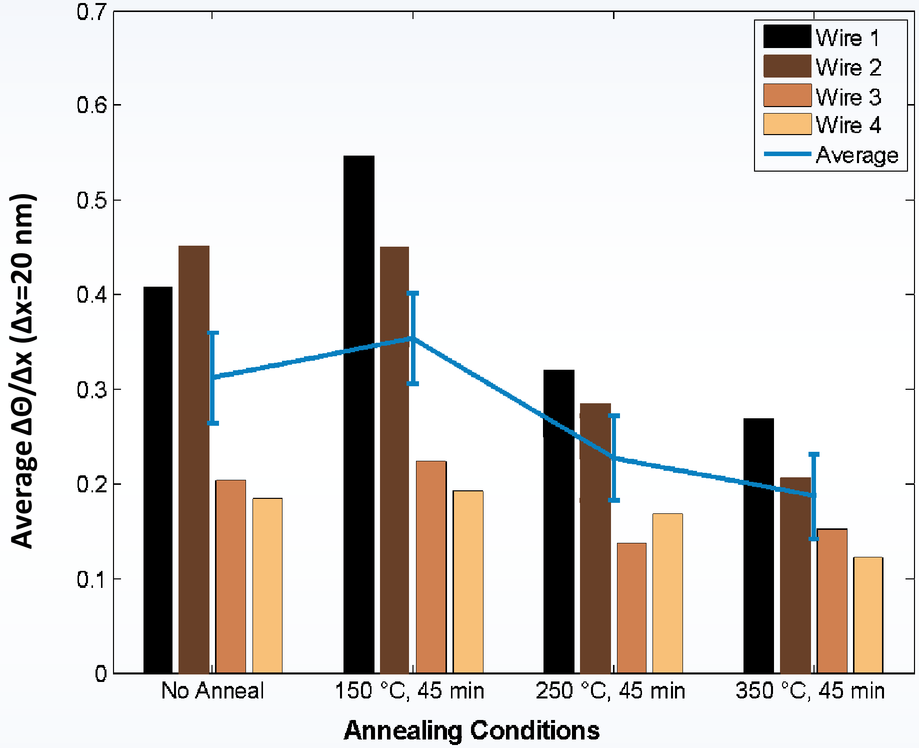
Same wire region analyzed



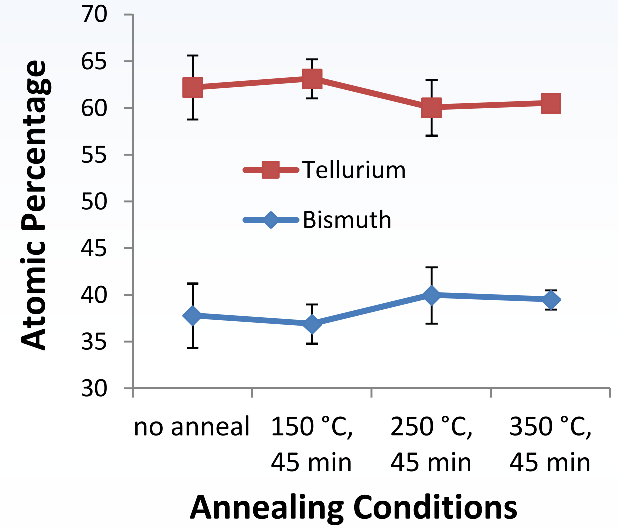


Ex Situ Annealing – Intragrain Crystallinity Analysis of Multiple Wires

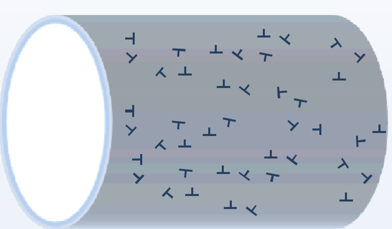
Dislocation Induced Disorder for all Wires under Annealing Conditions (with bulk Bi_2Te_3)



EDS Data



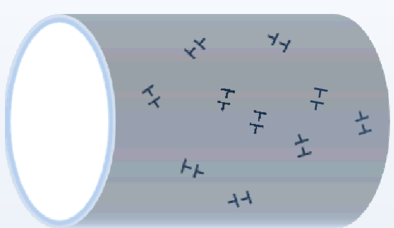
Stoichiometry Maintained since annealing done with bulk Bi_2Te_3 in ampoule



Decrease in Intragrain Disorder

→

Progress within Recovery Phase



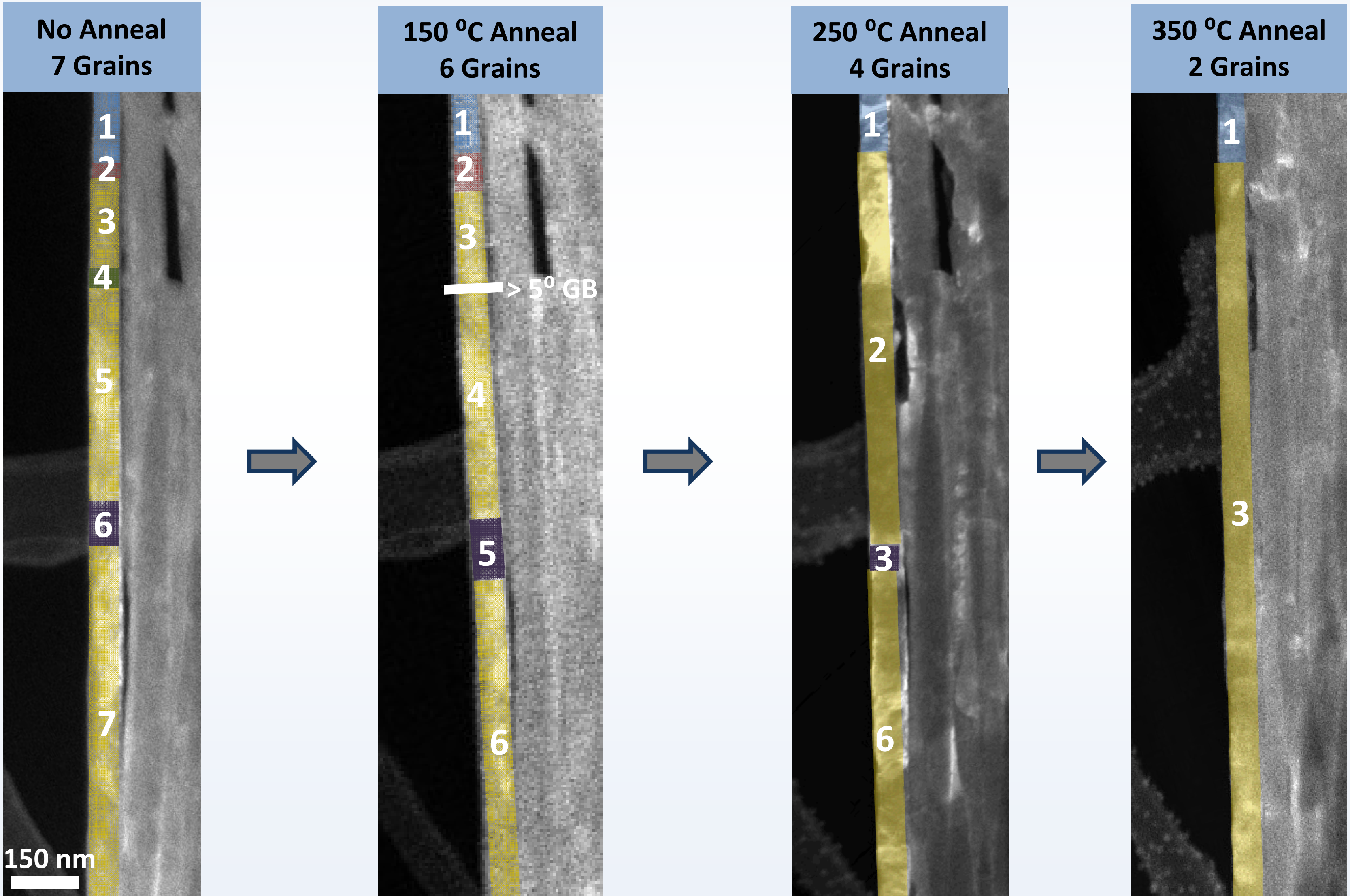
What about the recrystallization stage?

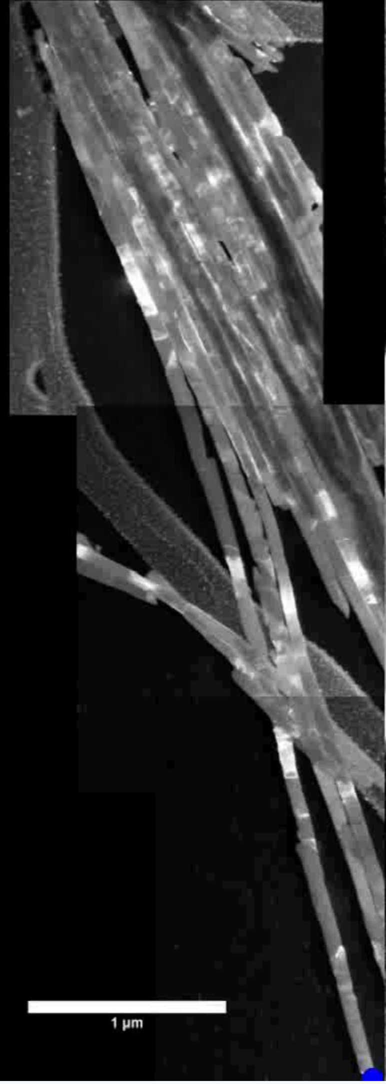
Ex-Situ Annealing: Recrystallization Stage Analysis

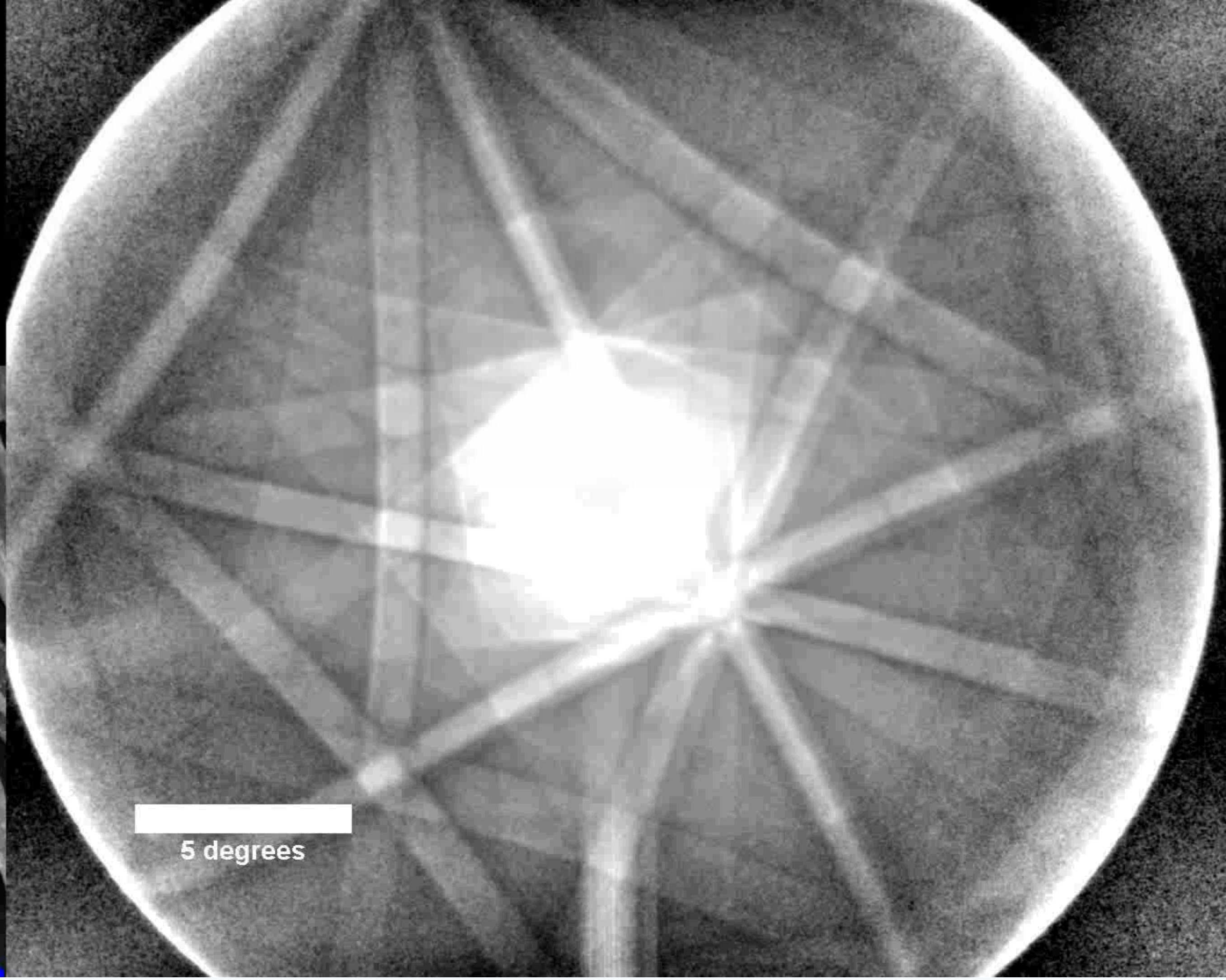
Only large angle GB (> 5°) being considered

Within 10° of [0 0 1] Zone, C-planes ~parallel to wire axis

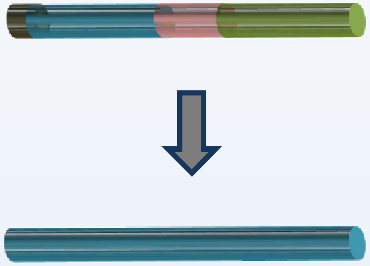
Oriented with other Zones





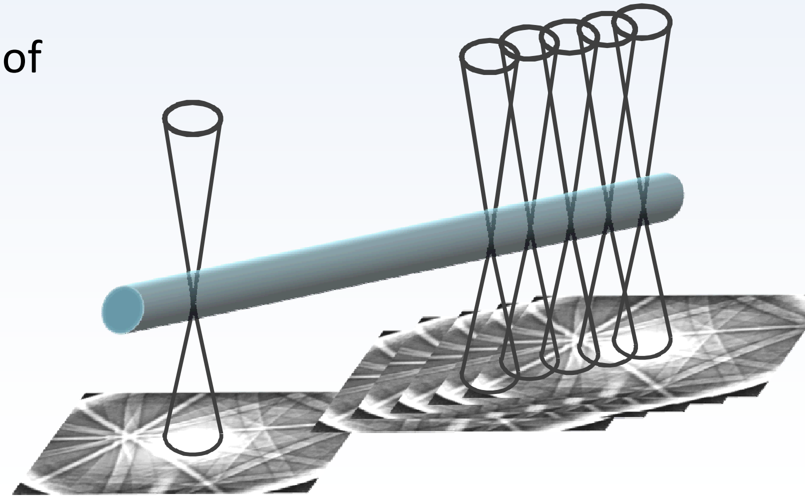


Wire annealed at 350 °C for 45 min with bulk Bi_2Te_3
5.2 µm long single grain
10.1° total difference between zone beginning and end



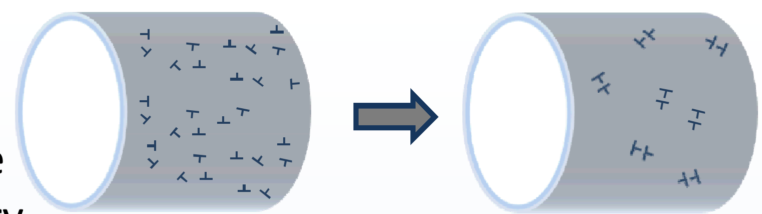
Conclusions

CBED/Mapping Technique Allows for the quantification of intragrain defects and observation of large angle grain boundaries at high spatial and angular resolution

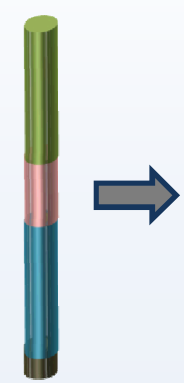


During annealing, Bi_2Te_3 NWs show significant improvement in crystallinity, similar to recovery and recrystallization phases

Significant decrease in zone tilt caused by defects and dislocations corresponding to recrystallization phase



Wires with multiple grains often become single grain upon annealing corresponding to recovery phase (most start with very few large angle grain boundaries)



Similar to the annealing of bulk deformed materials. After annealing with bulk Bi_2Te_3, NWs with grains of many microns long with very few intragrain defects result. Significantly higher ZT is expected.

Acknowledgements

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