SAND2014-16401D

(1/3)<0 -1 1 1> Dislocations in Bi_2Te_3 Nanowires: Defect Crystallography and Relationship to 7-layer Bi_3Te_4 Defects

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Introduction

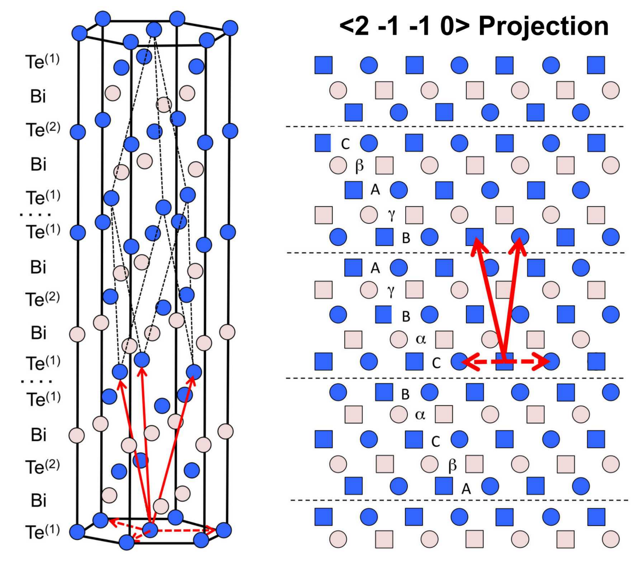
Bi_2Te_3, and its iso-structural siblings such as Bi_2Se_3 and Sb_2Te_3, have long been of interest for thermoelectric applications and in recent years have gained prominence in the burgeoning field of topological insulators. It is important to understand the nature of dislocations in these materials since such extended defects are closely connected to the materials growth processes and can affect the thermal and electronic transport properties. The layered structure and possibility for large Burgers vectors in these compounds also raises interesting questions regarding the manner in which dislocations might dissociate. Here, we discuss electron microscopic observations of *(1/3)<0-111>* dislocations in nanowires of Bi_2Te_3. There is significant interest in the growth of Bi_2Te_3-based nanowires, motivated by long-standing theoretical predictions of enhanced thermoelectric properties arising in low-dimensional structures of Bi_2Te_3 [1]. The analysis presented here was made in the course of a broader study exploring how growth and annealing conditions control the resulting crystallinity and internal microstructure in Bi_2Te_3-based nanowires [2,3].

Bi_2Te_3 Crystal Structure

Hexagonal setting: a=0.438 nm, c=3.05 nm

Rhombohedral setting: a_R=1.048 nm, α_R=24.1°

<2 -1 -1 0> Projection



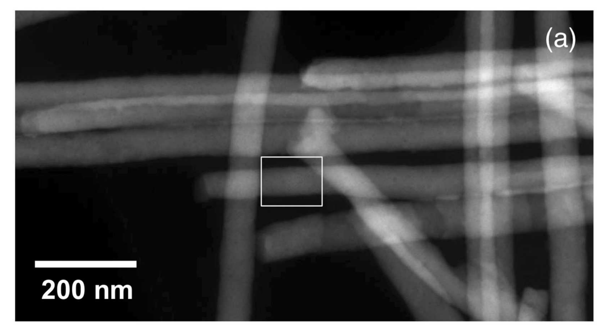
Dislocation Types

$\frac{1}{3}\langle 2\bar{1}\bar{1}0\rangle$ **b**=0.438 nm

$\frac{1}{3}\langle 0\bar{1}11\rangle = \langle 001\rangle_R$ **b**=1.048 nm

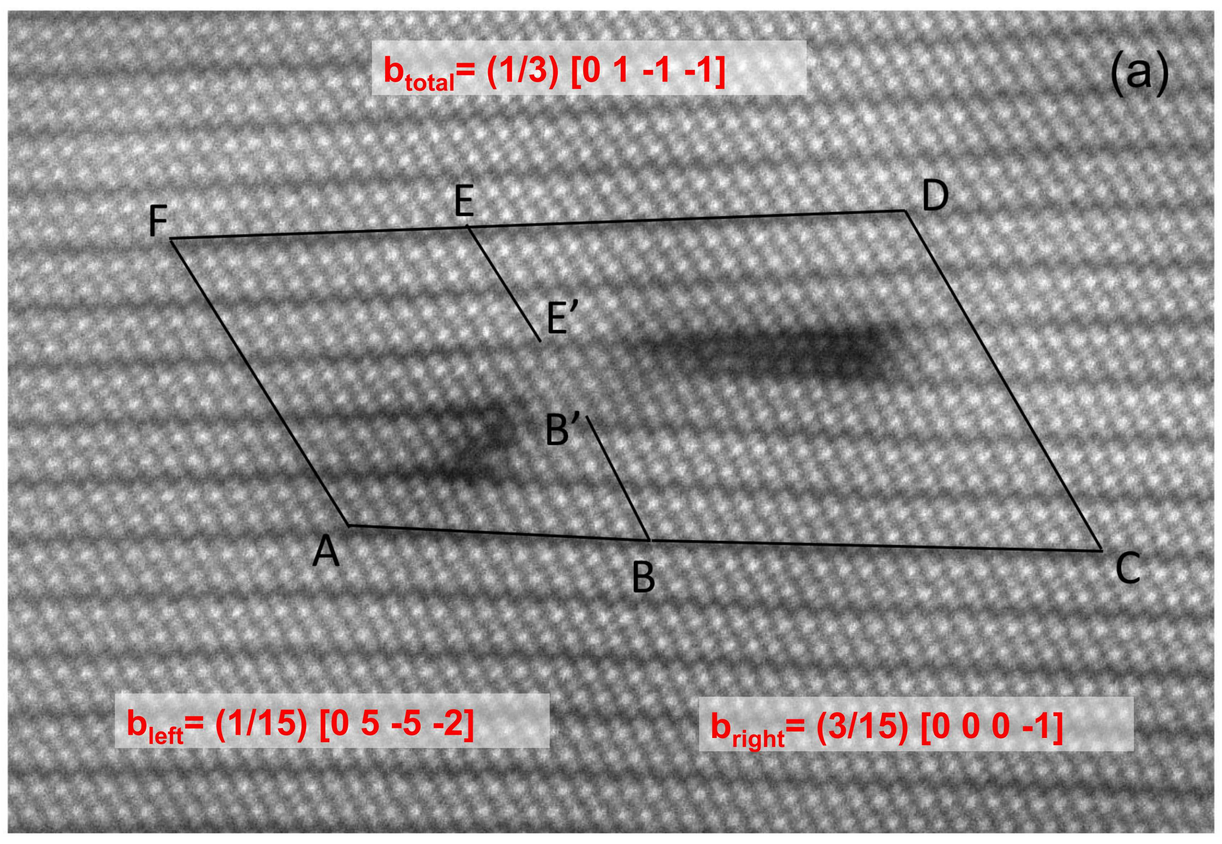
[1] L.D. Hicks, M.S. Dresselhaus, Phys. Rev. B 47 (24) (1993) 16631.
[2] S. J. Limmer, W. G. Yelton, M. P. Siegal, J. L. Lensch-Falk, Jamin Pillars, and D. L. Medlin, Journal of the Electrochemical Society 159 (4) D235-D239 (2012)
[3] M.P. Siegal, S.J. Limmer, J.L. Lensch-Falk, K.J. Erickson, D.L. Medlin, W.G. Yelton, C. Rochford, Journal of Materials Research 29 (2) 182-189 (2014).

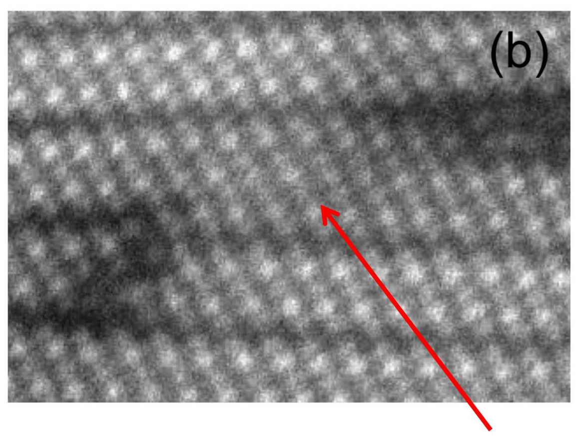
(1/3)<0-111> dislocations form with dissociated cores

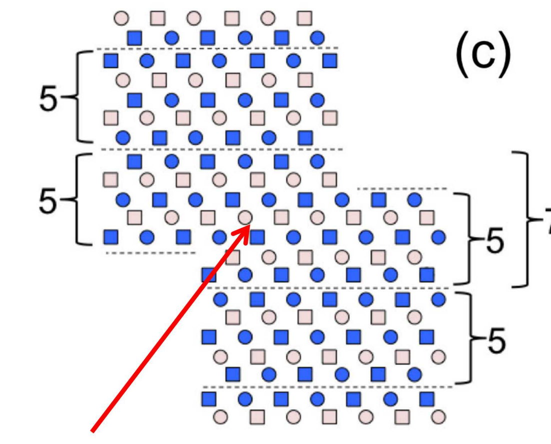


Circuit element	x-Component ($\frac{1}{6}[01\bar{1}0]$)	y-Component ($\frac{1}{3}[0001]$)	z-Component ($\frac{1}{6}[2\bar{1}\bar{1}0]$)
(a) Total dislocation (circuit ACDFA)			
AC	99	0	±1
CD	−30	6	0
DF	−96	0	0
FA	25	−5	±1
Sum:	−2	1	0
	$b = \frac{1}{3}[01\bar{1}\bar{1}]_H = [00\bar{1}]_R$		
	$\|b\| = 1.048$ nm		
(b) Left partial dislocation (circuit ABEFA)			
AB	39	0	±1
BB'	−10	2	0
B'E'	−7	≈7/5	±1
E'E	−10	2	0
EF	−39	0	±1
FA	25	−5	±1
Sum:	−2	≈2/5	0
	$b \approx \frac{1}{15}[05\bar{5}\bar{2}]_H = \frac{1}{5}[11\bar{4}]_R$		
	$\|b\| = 0.479$ nm		
(c) Right partial dislocation (circuit BCDEB)			
BC	60	0	0
CD	−30	6	0
DE	−57	0	±1
EE′	10	−2	0
E′B′	7	≈−7/5	±1
B′B	10	−2	0
Sum:	0	≈3/5	0
	$b \approx \frac{3}{15}[000\bar{1}]_H = \frac{1}{5}[\bar{1}\bar{1}\bar{1}]_R$		
	$\|b\| = 0.610$ nm		

For the **FS/RH** sign convention, with the dislocation line direction defined as positive out of the board, the Burgers vector, ***b***, is the negative of the vector sum of the individual circuit elements referenced to the perfect crystal

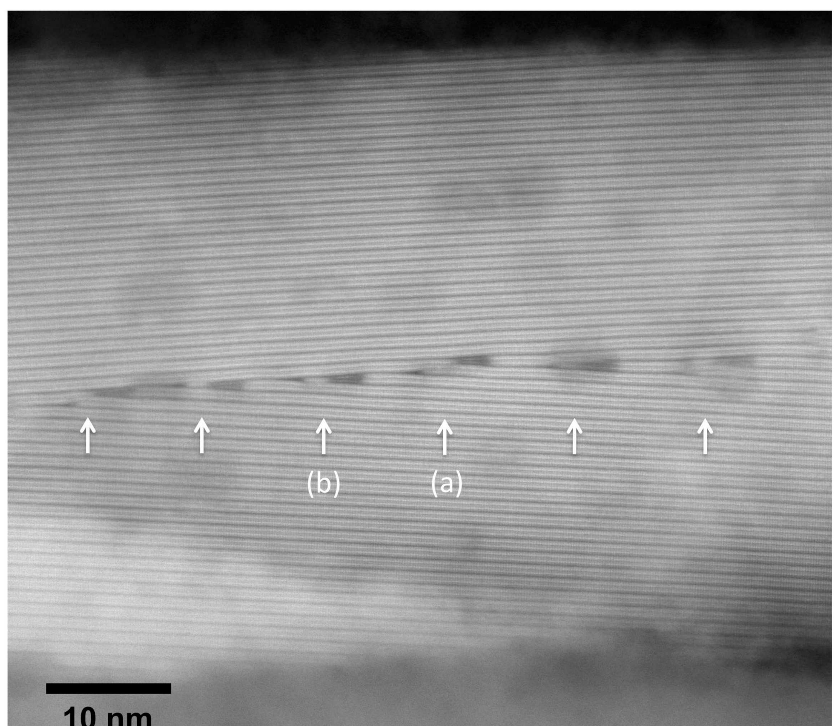


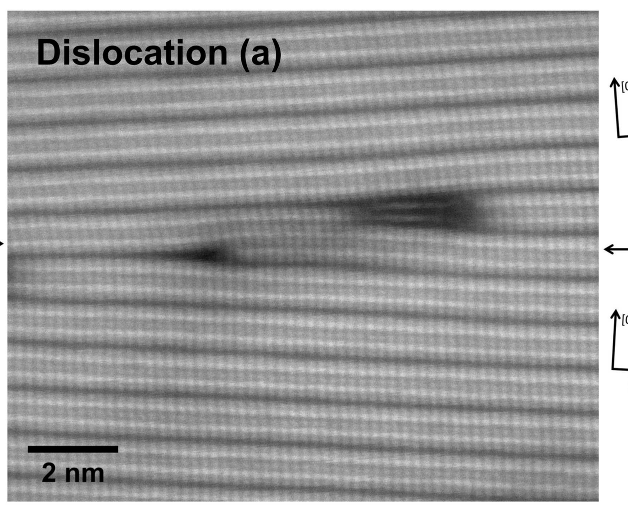


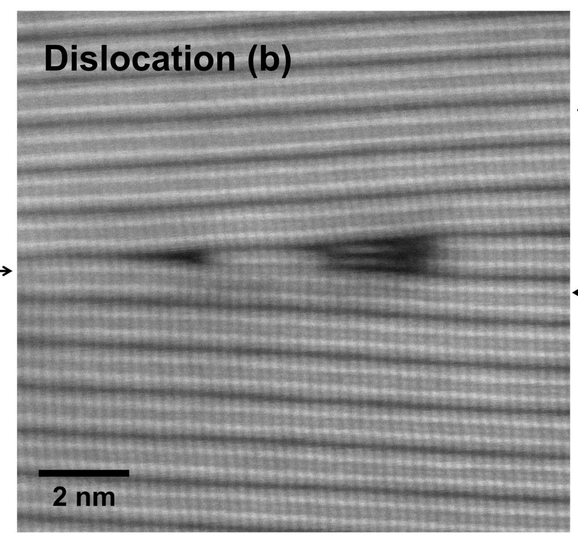


Core Structure:
Bi_3Te_4 7-layer fault

Array of (1/3)<0-111> dislocations at a low angle grain boundary

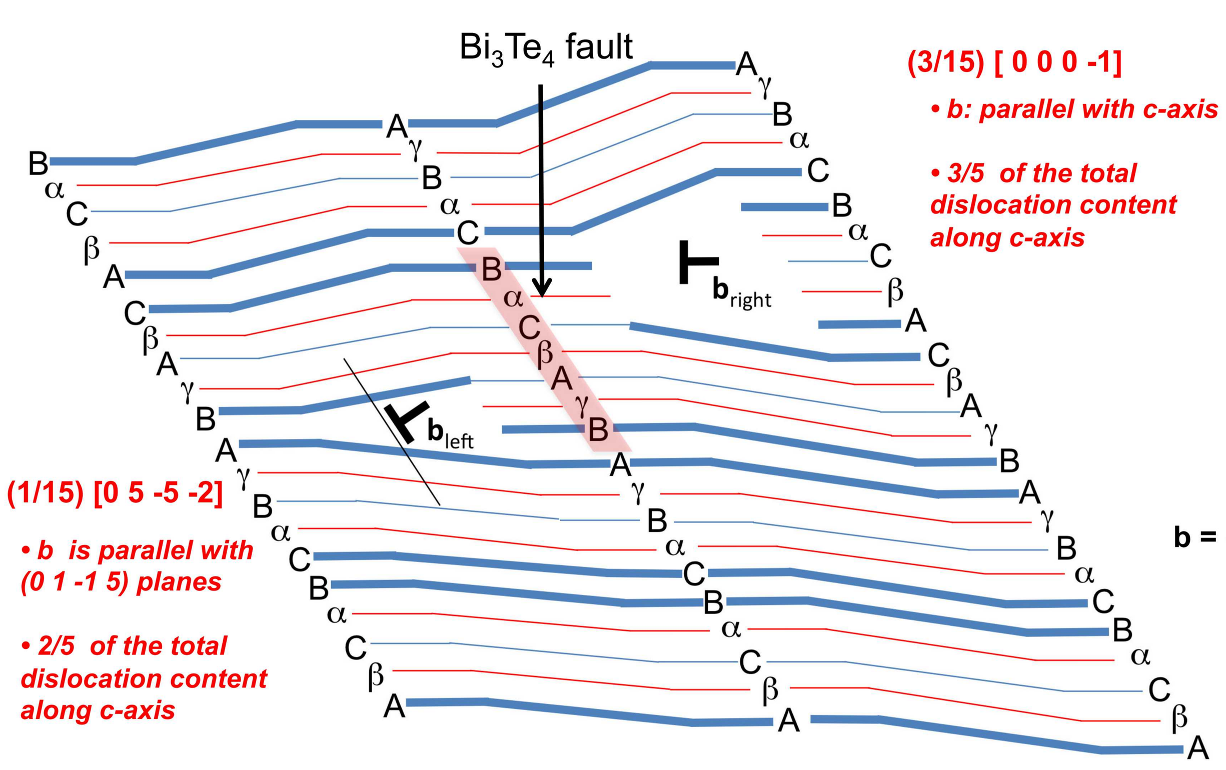






HAADF-STEM image of a Bi_2Te_3 nanowire imaged along a *<10-10>* orientation. A low angle grain boundary, which is vicinal to the (0001) planes, runs horizontally across the middle section of the wire. The 5.5° tilt misorientation between the two grains is accommodated by an array of dissociated *(1/3)<0-111>* dislocations, indicated by the arrows.

Dissociation Mechanism



(3/15) [0 0 0 -1]

- *b: parallel with c-axis*
- *3/5 of the total dislocation content along c-axis*

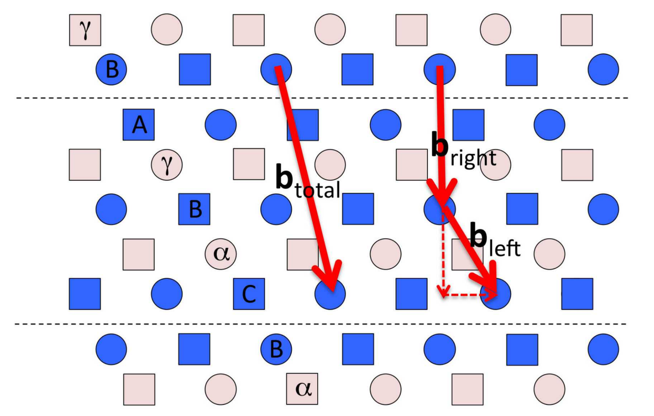
(1/15) [0 5 -5 -2]

- *b is parallel with (0 1 -1 5) planes*
- *2/5 of the total dislocation content along c-axis*

Horizontal component: (1/3) [01 -1 0]

- *analogous to Shockley partial.*
- *avoids fault in stacking resulting from additional 2 planes at Bi_3Te_4 fault*

Reduced strain energy with dissociation



b = (1/3) [0 1 -1 -1] → (1/15) [0 5 -5 -2] + (3/15) [0 0 0 -1]

$b^2 > b_1^2 + b_2^2$

109.8 Å² > 22.9 Å² + 37.2 Å² =60.2 Å²

Separation of the partials must occur through non-conservative climb-dissociation process.

Resulting 7-layer, Bi_3Te_4 fault provides mechanism to accommodate Te loss during annealing.

Experimental Methods

Bi_2Te_3 nanowires were prepared by electroplating into nanoporous anodic aluminum oxide (AAO) templates using procedures similar to those reported in [1]. AAO templates were formed by anodizing Al(Nd)/W film stacks deposited on silicon wafers. Anodization was conducted at 40 V and 1 °C in 3 wt% oxalic acid. After fully anodizing the Al(Nd) layer, the interfacial WO_3 layer was removed in a 0.2 M pH 7 phosphate buffer, and the pores were widened to ~ 75 nm in 5 wt.% H_3PO_4 at 30 °C. The nanowires were grown in the AAO nanopores by pulsed-current electrochemical deposition using the bath described by Banga *et al.* (6 mM $Bi(NO_3)_3$, 7 mM Na_2TeO_3, 0.3 M L-tartaric acid and 2 M HNO_3) [2]. We employed an on-current of -20 mA/cm² applied for 0.1 s, followed by an off-period (no current) of 0.9 s, repeating this cycle for 50 minutes. The solutions were sparged with N_2 for a minimum of 20 minutes prior to deposition and blanketed with N_2 during deposition.

To form freestanding arrays of nanowires, the AAO template was removed by etching in de-aerated 5 wt% H_3PO_4 solution at 30 °C for 6 hours with N_2 bubbling. After etching, the samples were rinsed repeatedly with deionized water, and then isopropanol. Finally, the samples were dried with supercritical CO_2 (Samdri-PVT-3D critical point dryer, Tousimis). The freestanding nanowire arrays were annealed at 300 °C for 30 min in an atmosphere of Ar-3% H_2 flowing at ~100 sccm. The specimens for electron microscopic observation were prepared by dispersing the nanowires onto holey carbon support grids by ultrasonication in isopropyl alcohol. Observations were conducted using an aberration-corrected FEI Titan TEM operated at 300 keV in scanning mode using a high angle annular dark field (HAADF) detector.

[1] Limmer SJ, Yelton WG, Siegal MP, Lensch-Falk JL, Pillars J, Medlin DL (2012) Electrochemical deposition of $Bi_2(Te,Se)_3$ nanowire arrays on Si. Journal of the Electrochemical Society 159 (4):D235-D239.

[2] Banga D, Lensch-Falk JL, Medlin DL, Stavila V, Yang NYC, Robinson DB, Sharma PA (2012) Periodic Modulation of Sb Stoichiometry in $Bi_2Te_3/Bi_{2-x}Sb_xTe_3$ Multilayers using Pulsed Electrodeposition. Crystal Growth & Design 12 (3):1347-1353

Conclusions

We have discovered *1/3<0-111>*-type dislocations in Bi_2Te_3 nanowires. Because these dislocations possess a large Burgers vector component along the c-axis, they are well suited to accommodate intergranular misorientations at grain boundaries with inclinations vicinal to {0001}. Here, we observed such a dislocation array at a grain boundary in an electrodeposited and annealed nanowire. We would also expect such dislocations to arise at low-angle grain boundaries in Bi_2Te_3 grown or consolidated by other methods, particularly those that lead to lamellar grain morphologies and <0001> textures, as occur in film growth and pressed powders. The observed dislocations form in a dissociated configuration consisting of two partial dislocations that separate a local 7-layer defect region, consistent with a single *septuple* unit of Bi_3Te_4. Analysis of the geometric properties of the partial dislocations helps to explain the local stacking arrangements and possibilities for core-rearrangements. The dissociation likely occurs to reduce the strain energy of the full *1/3<0-111>* dislocation, which has a remarkably large Burgers vector (b=1.048 nm) encompassing the width of a full Bi_2Te_3 quintuple unit. These observations suggest a mechanism for accommodating tellurium deficiency by the heterogeneous nucleation of septuple units at the cores of pre-existing *1/3<0-111>* dislocations.

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