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Preparation of Bismuth Telluride Specimens for TEM

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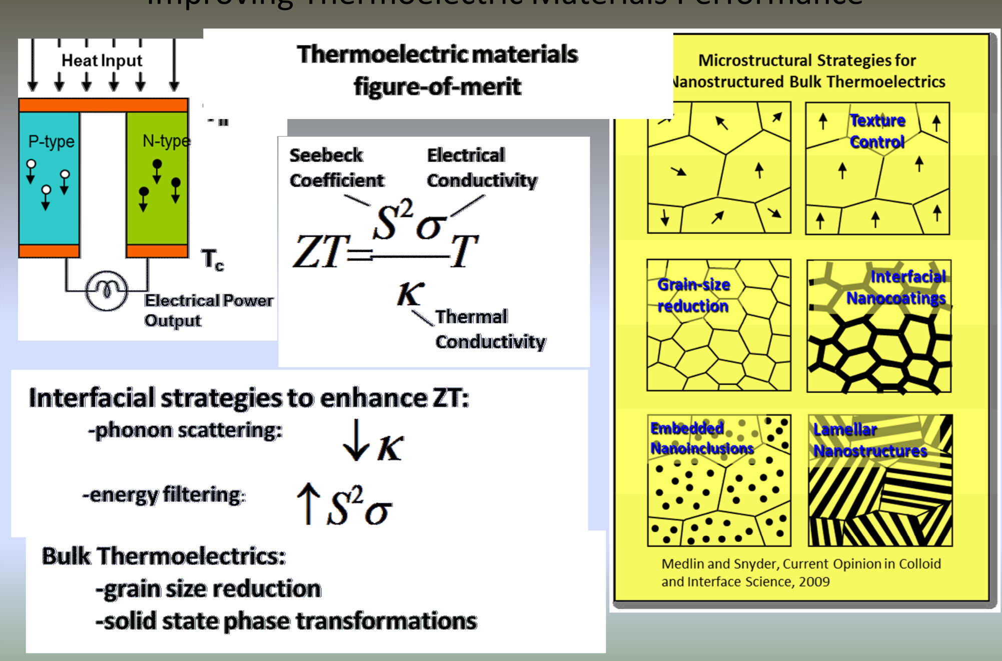
Introduction

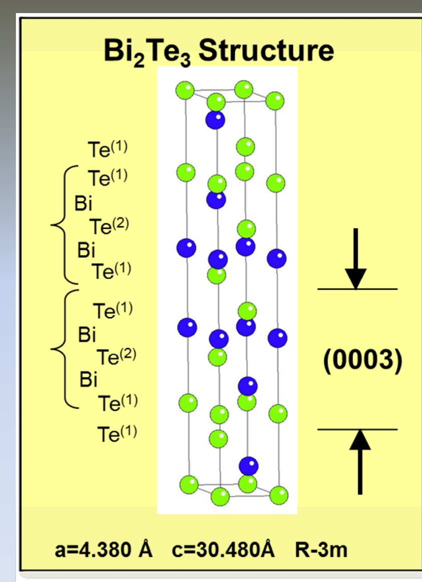
Bismuth telluride (Bi_2Te_3) and its alloys are known as an essential class of thermoelectric material. How well a thermoelectric material works is dependent on electrical and thermal conductivity, change in temperature, and the material's Seebeck coefficient. Electrical and thermal conductivity can be affected by defects in the material. Thus, there is much interest in the basic understanding the microstructures of these materials since extended defects, such as dislocations and grain boundaries, have important effects on the electronic and thermal transport properties that control the energy conversion efficiency [1]. One challenges in the preparation of TEM specimens for telluride-based materials is their sensitivity to ion-milling artifacts. For instance, nanoscale defect arrangements have been shown to form in lead telluride (PbTe) specimens prepared under aggressive ion milling conditions if cooling and power density is not suitably controlled [2]. Here, we investigate the preparation of Bi_2Te_3 TEM specimens using different methods and conditions to help clarify the potential for artifacts in Bi_2Te_3 specimens prepared by ion milling.

[1] D.L. Medlin and G.J. Snyder, "Interfaces in Bulk Thermoelectric Materials" Current Opinion in Colloid and Interface Science 14 (2009) 226-235. doi: 10.1016/j.cocis.2009.05.001.
[2] J. L. Lensch-Falk, J.D. Sugar, M.A. Hekmaty, D.L. Medlin, "Morphological Evolution of Ag_2Te Precipitates in Thermoelectric PbTe" Journal of Alloys and Compounds 504 (2010) 37-44, doi: 10.1016/j.jallcom.2010.05.054.

Tailoring and Characterizing Microstructure is important to Improving Thermoelectric Materials Performance



Background for Bi_2Te_3



Bismuth Telluride possesses a layered crystal structure consisting alternating Bi and Te planes.

In practical thermoelectric devices, Bi_2Te_3 is typically alloyed with Sb_2Te_3 for p-type legs and Bi_2Se_3 for n-type legs.

Weak van der Waals bonding between the $Te^{(1)}$-$Te^{(1)}$ layers leads to easy cleavage fracture along the (0001) type planes.

This poses challenges for TEM specimen preparation since the material is quite fragile. Very gentle handling and use of support rings is essential.

Nanoscale Striations: Intrinsic or Artifact?

Fine-scale contrast modulations, or striations, are often observed in TEM specimens of Bi_2Te_3 and its alloys prepared using energetic methods such as ion milling and FIB. These modulations typically have periodicities on the order of 10 to 20 nm and exhibit strong diffraction contrast that can be imaged in dark-field TEM using, for instance, {1,0,-1,5} type reflections. In the literature, these contrast features have been interpreted as "natural nanostructures" arising from strain modulations intrinsic to the material [1,2]. An alternative explanation is that the features arise as artifacts from the TEM specimen preparation.

To explore this question more deeply, in this study we compared observations of Bi_2Te_3 specimens prepared under intentionally aggressive ion milling conditions (high beam energy and current and steep milling angle) with specimens prepared by the more gentle conditions afforded by electropolishing.

[1]N. Peranio, O. Eibl, J. Nurnus, Journal of Applied Physics 100, 114306 (2006).
[2]N. Peranio and O. Eibl, Journal of Applied Physics 103, 024314 (2008).

Current Research

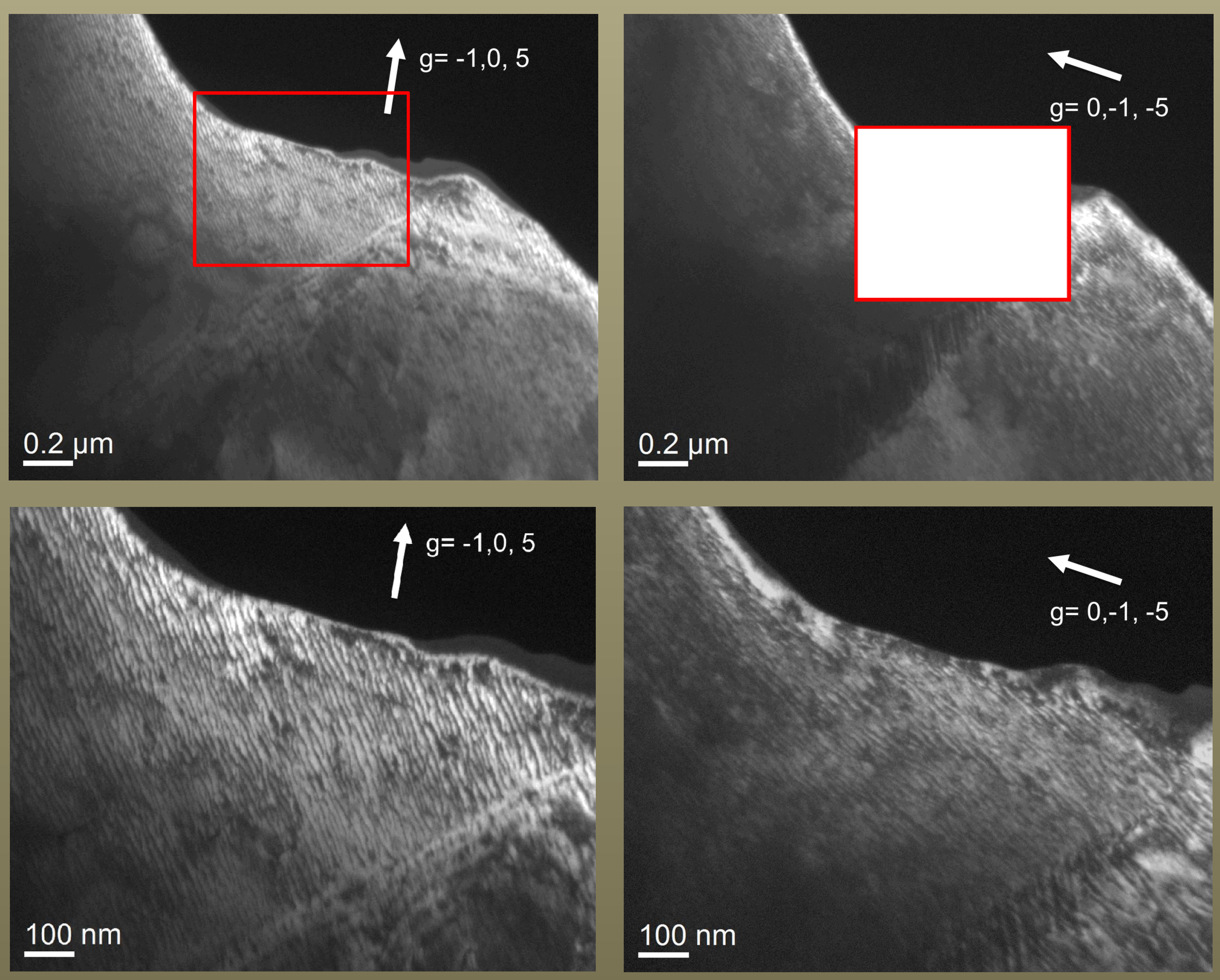
Understanding interfacial properties, boundaries and material nanostructures is crucial in understanding and improving thermoelectric materials. In previous work with Bismuth Telluride (Bi_2Te_3) focus was given to comparing Ion Milled samples to electropolished samples. The comparison showed the nature of the fine-scale contrast modulations, or striations were not natural but man made. For both techniques the sensitivity of the material was apparent during the specimen preparation process. Bi_2Te_3 is very fragile and readily fractures as the sample gets thinner, and thus care must be taken from start to finish.

Samples for this experiment are from N-Type, Bi_2Te_3 material that is less than 0.1% Te rich (NIST Standard Reference material #3451). For all samples in this project cutting, mechanical thinning, and mechanical polishing was identical. Backing/support rings were added to all samples to minimize cracking, with Au rings used for electropolished specimens and Molybdenum rings were added to Ion Milled specimens.

In previous work the method of Argon Ion Milling with initial thinning conducted at θ=10°, 5.0 kV and 5.0 mA with a final milling @ θ=6°, 1.5 kV and 3.0 mA resulted in striations.

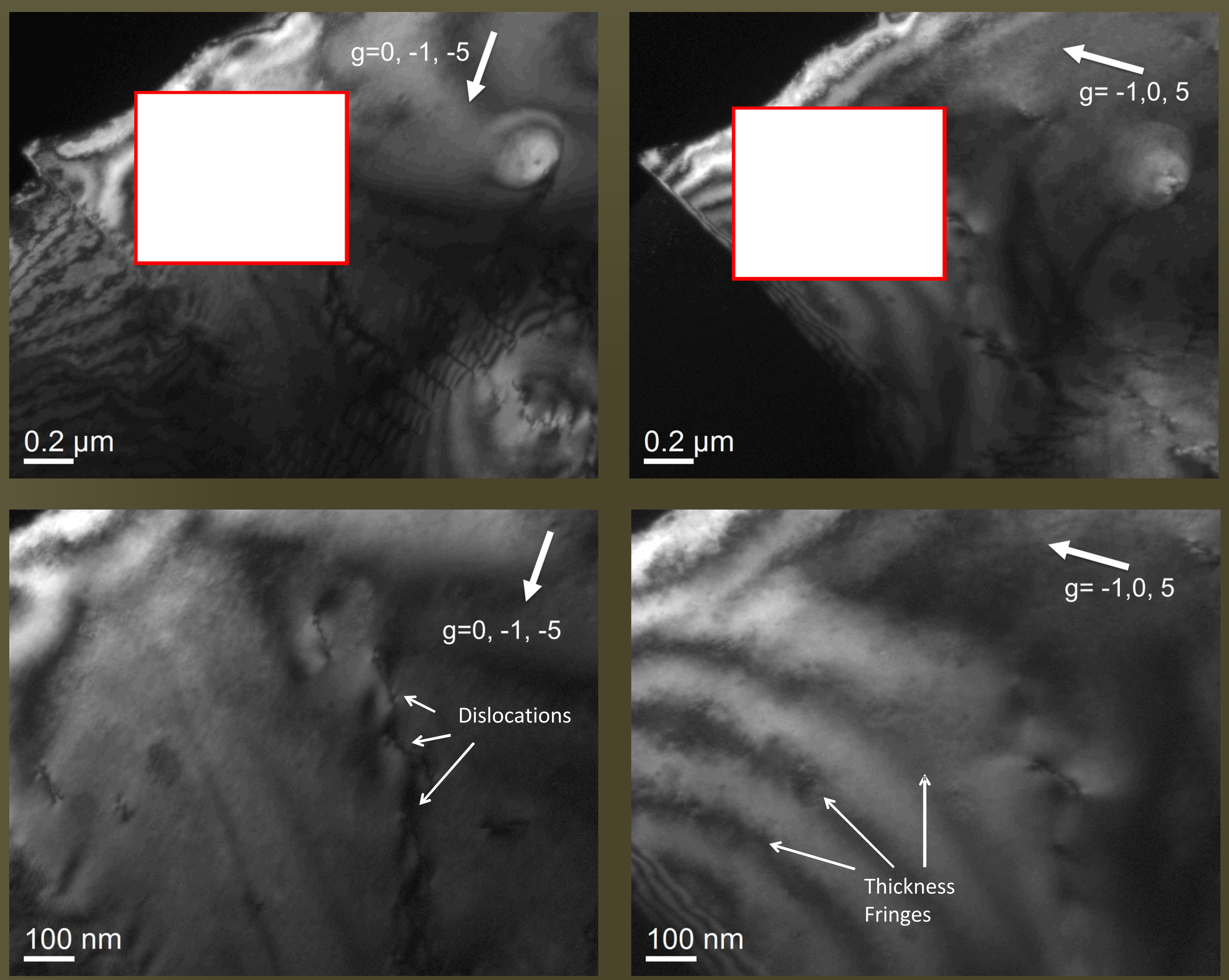
In practical applications thermoelectric materials need a process that allow us to look at the material with process inclusions. Our work is focused on increasing our ability to create striation free TEM samples from multiple methods with an increased functional area. Electropolishing and Ion Milling both show promise in producing striation free samples.

Ion Milled Specimen



Above: Dark Field TEM images from an Ion milled specimen prepared under aggressive conditions show fine-scale contrast modulations, or striations, with periodicities on the order of 10 to 20 nm. Preparation conditions: Ar+ ion sputtering with liquid N_2 cooling using a Fischione Model 1010 ion mill. Initial thinning was conducted at θ=10°, 5.0 kV and 5.0 mA with a final milling @ θ=6°, 1.5 kV and 3.0 mA. Specimen imaged near a [5,-5,1]zone under strong-beam dark field conditions.

Electropolished Specimen



Above: The fine scale striations are not observed in electropolished specimen. Preparation conditions: Electropolishing using a Fischione, Model 120 twin jet polisher. Electrolyte consisting of 53% water, 38% glycerol, 5% sodium hydroxide, and 4% tartaric acid. The electrolyte was set in an ice bath and cooled to 2° C, and electropolished at 25V and 35mA. Specimen imaged near a [5,-5,1] zone under strong-beam dark field conditions.

Conclusions

- We observed fine scale striations in Bi_2Te_3 TEM specimens prepared under aggressive Ion Milling conditions.
- Electropolished samples of the same material and equivalent diffracting conditions do not show these striations.
- This result is consistent with these striations being an artifact of Ion Milling.
- These results emphasize that caution must be applied when preparing TEM specimens of Bi_2Te_3 or related materials by energetic processes such as Ion Milling and FIB.

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