Ion Beam Induced Artifacts in Lead-Based Chalcogenides

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Abstract
Metal chalcogenides have attracted great attention because of their broad applications. It has been well acknowledged that microstructure can alter the intrinsic properties and performance of metal chalcogenides. The structure–property–performance relationships can be investigated at atomic scale with scanning transmission and transmission electron microscopy (STEM and TEM). Nevertheless, careful specimen preparation is paramount for accurate analyses and interpretations. In this work, we compare the effects of a variety of well-established TEM specimen preparation methods on the observed microstructure of an ingot stoichiometric lead telluride (PbTe). Most importantly, from aberration corrected STEM and first principles calculations, we discovered that argon (Ar) ion milling can lead to surface irradiation damage in the form of Pb vacancy clusters and self-interstitial atom (SIA) clusters. The SIA clusters appear as orthogonal nanoscale features when characterized along the <001> crystal orientation of the rock salt structured PbTe. This obfuscates the interpretation of the intrinsic microstructure of metal chalcogenides, especially lead chalcogenides. We demonstrate that with sufficiently low energy (300 eV) Ar ion cleaning or appropriate high-temperature annealing, the surface damage layer can be properly cleaned and the orthogonal nanoscale features are significantly reduced. This reveals the materials’ intrinsic structure and can be used as the standard protocol for future TEM specimen preparation of lead-based chalcogenide materials.

Key words: aberration-corrected STEM, beam effects, damage, ion irradiation, sample prep, thermoelectric materials

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Introduction
Metal Chalcogenides are a well-recognized group of inorganic materials that always contain one or more of the chalcogen anions. They have shown great potential in applications such as topological insulators (Hasan & Kane, 2010), solar cells (Grätzel, 2009), tunable diode lasers (Preier, 1979), superconductors (Mizuguchi & Takano, 2010), and thermoelectrics (Tan et al., 2016). It has been well-demonstrated that microstructural features such as point defects (Page et al., 1997; Zhao & Burda, 2012), dislocations (John & Zogg, 1999; Liu et al., 2014), grain boundaries (Krusin-Elbaum et al., 2007; Li et al., 2014), and precipitates (Girard et al., 2011; Luo et al., 2018b) can greatly affect the properties and performance of metal chalcogenides. Particularly, for thermoelectric applications, microstructural features at different length scales can modify the electron and phonon transport of the materials and result in high energy conversion efficiency (He et al., 2013; Kim et al., 2015; Pei et al., 2016; Sarkar et al., 2018; Luo et al., 2018a).

Investigating the microstructure in metal chalcogenides can be challenging because different structural features exist over various characteristic length-scales. Analytical Scanning/Transmission Electron Microscopy (S/TEM), however, serves as a vital toolset for investigating these structures from the atomic scale to the microscale. S/TEM can provide information about materials such as crystal structure, composition of atomic defect species and their concentration, dislocation density and related strain field, grain boundary configuration and composition, as well as precipitate composition, structure and distribution (Pennycook et al., 2006; Kisielowski et al., 2008; Lu et al., 2012). Proper TEM analysis requires a specimen to be, “electron transparent”, meaning that the areas observed with TEM must have a thickness of approximately 20–100 nm (Ayache et al., 2010). As a result, the millimeter, or even centimeter, sized ingot sample must go through a lengthy TEM sample preparation process. Different artifacts can be induced during specimen preparation depending on which method is used, which can make the interpretation of TEM images difficult (Carter & Williams, 2009). Discerning between intrinsic material features and potential artifacts is vital in determining the structure–property–performance relationship in metal chalcogenides.

To obtain an electron transparent specimen for S/TEM characterization, specimen preparation methods need to be strategically chosen based on the materials properties and the type of microstructural features being investigated. There are five specimen preparation methods that are suitable for common solid-state metal chalcogenide materials: (1) crushing, (2) twin jet electropolishing, (3) ultramicrotomy, (4) mechanical polishing followed by Ar ion milling (abbreviated to ion milling in this...
Materials and Methods

Synthesis

High purity (>4N) single elements of lead (Pb), tin (Sn), and tellurium (Te) were weighted according to the nominal compositions and vacuum sealed in silica tubes, which were then transferred to a computer-controlled furnace and melted at 1,100°C for 6 h. The furnace was then switched off to let the molten material cool down naturally to room temperature.

First Principles Calculations

First principles calculations were performed to reveal the defect formation energy in PbTe system. The calculations were based on density functional theory within the generalized gradient approximation and the projector augmented wave method as implemented in the VASP code (Kresse & Furthmüller, 1996). The plane-wave basis-set cutoff was set to 450 eV. Convergence with respect to self-consistent iterations assumed the residual forces were <0.02 eV/Å. In the defect calculations, the lattice parameters were fixed to the calculated bulk values, but all of the internal coordinates were fully relaxed. Calculations for Pb and Te vacancy and interstitial defects were performed using a 3 x 3 x 3 conventional cell with 216 atoms. The formation energy of a vacancy defect is defined as $E_f(V) = E_{tot}(V) - E_{pure} + \mu(X)$, where $E_{tot}(V)$ and $E_{pure}$ are respectively, the total energies of a supercell containing the defect X and of a supercell of the perfect bulk material; $\mu(X)$ is the atomic chemical potential of species. Similarly, for the interstitial defects, the formation energy is calculated as $E_f(I) = E_{tot}(I) - E_{pure} - \mu(X)$, where $E_{tot}(I)$ is the total energies of a supercell containing the interstitial defect X. Here, for the Pb-rich condition, the Pb chemical potential $E_{Pb_{bulk}}$ is the total energy of Pb bulk and corresponding Te chemical potential is $E_{Te} = E(PbTe) - E(Pb_{bulk})$. Similarly, for the Te-rich condition, the Te chemical potential $E_{Te_{bulk}}$ is the total energy Te bulk and corresponding Pb chemical potential is $E(Pb) = E(PbTe) - E_{Te_{bulk}}$, where $E(PbTe)$ is the total energy from rock salt PbTe. Though we consider the Te-rich and Pb-rich conditions, the total formation energy results of a vacancy and a corresponding interstitial do not depend on these conditions.

Specimen Preparation Methods

Crushing

Thermoelectric samples were crushed using an agate mortar and pestle. First, the ingot specimen was immersed into liquid nitrogen and cooled down to cryogenic temperature. It was then crushed and ground into fine powders with the mortar and pestle. This powder was collected and dispersed into methanol. The solution is sonicated and drop-cast onto a TEM grid with carbon film and dried in a fume hood.

Twin jet Electropolishing

The bulk specimen ingot was first cut into thin slices (<1 mm) using a wire saw with abrasive diamond slurry. The slice was mechanically thinned and polished with a wheel grinder to approximately 100 μm in thickness and then cut into 3 mm diameter using an ultrasonic disc cutter. Approximately 1 L of electrolyte was prepared with a molar ratio of KOH: glycerol: ethanol = 4: 1: 10. (Norr, 1963) The discs were then electropolished using a TenuPol-5 electrolytic thinning unit from Struers Inc., (Cleveland, OH, USA). Electropolishing was stopped when a
hole was formed at the center of the disc and the edges around the hole were electron transparent.

**Ultramicrotomy**

A small piece of PbTe was cleaned and mounted directly into the ultramicrotome with a sample chuck (Leica UC7 Ultramicrotome, Leica Microsystems, Wetzlar, Germany). To avoid destroying the sample with the sample chuck clamp, minimal pressure was used when securing the sample in place. A very small blockface was formed utilizing a glass knife and ultrathin 40–50 nm slices were sectioned with a 35° diamond knife.

In an attempt to increase stability another piece of PbTe was embedded in an epoxy resin and mounted securely in the ultramicrotome. The sample was then exposed from the epoxy and a block face was formed with a glass knife. Ultrathin 40–50 nm slices were then gathered utilizing a 35° diamond knife.

**Ion Milling**

Similar to twin jet electropolishing, the bulk specimen was firstly diced into thin slices using an abrasive slurry wire saw and then thinned and polished with a wheel grinder to approximately 100 µm in thickness. The specimen was further thinned using a Gatan dimple grinder (Gatan Inc., Pleasanton, CA, USA), until the center of the specimen was <10 µm thick. Ion milling was carried out on a Fischione Model 1050 TEM Mill (E.A. Fischione Instruments, Inc., Export, PA, USA). The initial stage of ion milling was performed with the milling angle and energy of ±6° and 2.8 keV, separately, until a hole formed. The specimen was then cleaned at ±4° and 2 keV for 30 min. The entire ion milling procedure was performed at below −120°C with the help of a liquid nitrogen cooling stage.

**Low Energy Ar ion Cleaning**

This process was also performed using the Fischione Model 1050 TEM Mill. The Ar ion guns were set at ±4° and 300 eV and the stage was cooled to below −120°C using liquid nitrogen. Good results require over 70 min of cleaning.

**Focused Ion Beam (FIB) Thinning**

Specimen preparation via FIB thinning was performed using a FEI Helios Nanolab SEM/FIB (Thermo Fisher Scientific, Waltham, MA, USA). A thin slice was cut out with 30 kV focused Ga ion and then transferred to TEM grid using the Omniprobe lift-out technique (Oxford Instruments, Abingdon, United Kingdom). The transferred specimen was then further thinned and cleaned with sequential Ga ion gun voltages of 16 kV, 8 kV, 5 kV, and 2 kV.

**Scanning Transmission and Transmission Electron Microscopy**

Conventional/high-resolution TEM, High angle annular dark field (HAADF) and bright field (BF) STEM were used for imaging specimens prepared using the five different methods. A JEOL JEM-2100 FaSTEM (JEOL Ltd., Akishima, Tokyo, Japan) was used for conventional and high-resolution TEM as well as HAADF STEM imaging. A Hitachi HD-2300 Dual EDS Cryo STEM (Hitachi, Chiyoda, Tokyo, Japan) was used for HAADF STEM imaging and Energy Dispersive Spectroscopy (EDS) (Dual EDS detectors, model number 4474B-4NES-BE, Thermo Scientific, Madison, Wisconsin). A JEOL ARM200CF aberration-corrected TEM was used for atomic resolution HAADF and BF STEM imaging.

The in situ heating experiment was performed on JEOL JEM-2100 FaSTEM with a Gatan 652 heating in situ holder (JEOL Ltd, Akishima, Tokyo, Japan; Gatan Inc., Pleasanton, CA, USA). The specimen was heated from room temperature to 100°C with 5°C/min ramping rate, kept at 100°C for 5 min, the heated from 100 to 220°C with 2°C/min ramping rate.

**Results and Discussion**

**Effect of Ion Beam on Thermoelectric Materials**

TEM specimens of ingot stoichiometric PbTe have been prepared using crushing, twin jet electropolishing, ultramicrotomy, FIB thinning, and ion milling. Materials for these five different specimen preparation methods were obtained from the center of the same ingot in order to make sure the compositions of the specimens are consistent. TEM images of their characteristic microstructures are shown in Figure 1. Among these five specimen preparation methods, no ion–specimen interaction takes place in crushing (Fig. 1a), ultramicrotomy (Fig. 1b) or twin jet electropolishing (Fig. 1c) methods. Ion milling (Fig. 1d) and FIB thinning (Fig. 1e) involve high energy (>1 keV) ion–specimen interactions during specimen preparation processes. The PbTe specimens prepared by FIB thinning and ion milling show characteristic orthogonal nanoscale features with high number density. The featured structures appear as dark line segments, of approximately 3–10 nm in length and roughly 2–5 lattice fringes in width as shown in the inset figure of Figure 1d. The long sides are parallel to <001> crystal orientations. In contrast, no obvious nanoscale features were observed in PbTe specimens prepared by crushing, twin jet electropolishing or ultramicrotomy.

We expect consistent microstructure from different TEM specimens of the same ingot material, regardless of their specimen preparation methods. However, two sets of microstructures (with and without orthogonal nanoscale features) were observed based on how the specimen was prepared. This indicates that certain specimen preparation methods might either reveal the intrinsic structure of the material or generate surface artifacts. The involvement of ion–specimen interaction is the most pronounced difference between the two groups of specimen preparation methods with different microstructures. In order to test the effect of ion beam on the specimen, the TEM specimen prepared by twin jet electropolishing (Fig. 1c), in which no obvious nanostructure was observed, was then milled using 2.8 keV Ar ion beam at 6° for 25 min (microstructure shown in Fig. 1f). After Ar ion milling, a large number density of orthogonal nanoscale features similar to Figures 1d and 1e was again observed. The re-generation of orthogonal nanoscale features in twin jet electropolishing specimen after further ion milling provided evidence that the involvement of ion beam either generated these nanostructure features or helped reveal the intrinsic nanostructure features in PbTe.

Other than PbTe, tin telluride (SnTe), lead sulfide (PbS), and tin sulfide (SnS) are also common metal chalcogenides that are potential candidates for thermoelectric matrix materials. TEM specimens of these three materials were prepared by ion milling and TEM images were collected for each specimen along the [001] zone axis. Figure 2 demonstrates that the orthogonal nanostructure features can be observed in both PbTe and PbS, but not in SnTe and SnS. It is worth noting that the crystal structure of SnS is orthorhombic with a Pbnm space group (Tan et al., 2014) while the crystal structure of PbTe, SnTe, and PbS is cubic with a Fm3m space group. From what has been observed in these four examples and previous research (Lee et al., 2013, 2014; Zhao et al., 2014; Wei et al., 2016), the ion beam-related nanostructure features are more profound in lead chalcogenides compared to tin chalcogenides.
Reduction of the Nanoscale Features

Ion milling is one of the common methods for TEM specimen preparation as it generates large electron transparent areas. It has been reported that ion beam can have the effect of mixing different atoms into solid solution (Tsaur et al., 1980; Averback, 1986) as well as amorphization of crystalline materials (Pelaz et al., 2004). However, the nanoscale feature observed in lead chalcogenides is very regularly shaped, orthogonally orientated structures. It is counterintuitive to relate these features to ion beam effects. Based on the results in Figure 1, the orthogonal nanoscale features seem strongly related to ion–specimen interaction. It is necessary to determine whether these structures are intrinsic throughout the whole specimen or if they are surface artifacts generated during ion–specimen interaction. Lensch-Falk et al. (2010) have reported that in a more complicated metal chalcogenide system, PbTe–Ag3Te, nanoscale artifacts can be observed when the TEM specimen was prepared with several hours of high energy ion milling at room temperature. They also observed that these artifacts can be reduced with a shorter time, lower energy ion milling at cryogenic temperatures.

Several groups have demonstrated the effectiveness of low energy inert gas ion milling in removing the surface damaged layer or reducing the thickness of the damaged layer. This method can reduce surface roughness of the specimen, revealing the intrinsic material beneath while further reducing the specimen thickness, ultimately resulting in electron transparent areas (Barna et al., 1999; Giannuzzi, 2006; Jin et al., 2010; Mitome, 2012; Fischione et al., 2017). Low energy (<1 keV) inert gas (Ar) ion milling was performed to determine whether the nanoscale features are intrinsic structures or surface artifacts. Two TEM specimens (Ingot_PbTe_1 and Ingot_PbTe_2) from the same PbTe ingot were prepared using the ion milling method. A large number of nanoscale features were observed in Ingot_PbTe_1 as shown in Figure 3a. The nanoscale features have different shape and orthogonal orientations because the images in Figures 3a and 3b were collected in the [011] direction instead of [001]. Low energy (300 eV) Ar ion milling was then performed on this as-prepared Ingot_PbTe_1 for 35 min. The number of nanoscale features present visibly decreased, but were not eliminated, after 35 min of low energy ion milling treatment (Fig. 3b). Almost no obvious nanoscale features were observed when the sample was subjected to an additional 35 min of low energy ion milling (Fig. 3c). It is worth noting that further thinning of the specimen with low energy ion milling results in the complete removal of the very thin regions imaged in Figures 3b and 3c, and we could not take TEM images from the exact same areas before and after the low energy ion milling. Nevertheless, all data were obtained from the same specimen around similar areas. In order to demonstrate reproducibility of the cleaning effect, low energy (300 eV) Ar ion milling was then performed on another ingot PbTe specimen, Ingot_PbTe_2 for 70 min. Figure 3d depicts that a large number of orthogonal nanoscale features can be observed in the as-prepared Ingot_PbTe_2 specimen, however, after 70 min of...
low energy Ar ion milling, the specimen looks very clean and there is no contrast indicating notable features (Fig. 3e). The fact that these nanoscale features can be successfully reduced using low energy (300 eV) Ar ion milling strongly suggests that they are very unlikely to be intrinsic material structures but are surface damage artifacts from the ion beam thinning process. It has also been reported that ion milling or ion sputtering can create a damaged surface layer a few tenths of a micrometer thick (Palmetshofer, 1984), which also supports that these nanoscale features are highly susceptible to ion-bombardment induced surface damage. The schematics in Supplementary Figure S1 illustrate the proposed mechanism for eliminating the damaged surface layer. After high energy ion milling, a damaged layer appeared at the surface of the specimen. With 35 min of low energy (300 eV) Ar ion milling, the damaged surface layer is partially removed, explaining why fewer nanoscale features are present in Figure 3b. With 70 min total of low energy Ar ion milling, the damaged surface layer at electron transparent area of the specimen was mostly removed, revealing the clean microstructure shown in Figure 3c. Similarly, it has been shown in bismuth chalcogenides, especially Bi$_2$Te$_3$, high energy ion milling will create nanoscale artifacts that appear to be fringes. It has also been shown that these artifacts in Bi$_2$Te$_3$ can be reduced under less aggressive conditions (Aabdin et al., 2012; Homer & Medlin, 2012).

**Nature of the Nanoscale Features**

If, in fact, possible that the nanoscale features are surface damage artifacts, it is important to determine the nature of these features. In specific, the regular shape and orientation of the features must have an explanation. In situ heating experiment in TEM can reveal detailed structure evolution in real time. The vacuum environment inside of the TEM can also prevent the specimen from reacting with atmosphere. Here, we performed in situ heating on a partially cleaned ingot PbTe specimen. First, the entire sample was ion milled using a high energy Ar ion beam. The sample was then partially cleaned by limiting the rocking angle of the stage during low energy Ar ion milling. This leaves a region of the specimen untouched by the low energy Ar ion beam which should still have surface layer damage. As a result, we have found two regions with different microstructures in one specimen, as seen in Figure 4a. No orthogonal nanoscale features can be observed in the “clean” region where the surface damage layer was removed by low energy Ar ion milling. However, orthogonal nanoscale features can be observed in the “damaged” region from the blind area of the Ar ion beam.

The specimen was heated in situ from room temperature to 220°C. After the displayed temperature of the in situ heating system reached 220°C, the nanoscale features were observed to diminish in density and there are no noticeable features in the region of interest. As shown in Figures 4d–4f, no orthogonal nanoscale features can be observed after the in situ heating process. Supplementary Figure S2 demonstrates the microstructure of other parts of the specimen. Similarly, no obvious nanoscale features were found in other parts of the specimen after the heating process. The annihilation of the nanoscale features sheds light on the nature of these nanoscale features. Since 220°C is below the eutectic temperature of a Pb-Te binary system (Lin et al., 1989), if these features are nanoscale precipitates as has been hypothesized, the heating process would ideally result in either precipitate coarsening or formation of new nucleus of precipitates (Lifshitz & Slyozov, 1961; Wagner, 1961). In contrast, we observed the annihilation and elimination of these microstructures. This demonstrates that the orthogonal nanoscale features are highly possible to be point defects or dislocations instead of nanoscale precipitates.
Ion irradiation damage mechanisms have been extensively investigated in the nuclear engineering community. When a material is being struck by high energy ions, the collision will generate Frenkel pairs of vacancies and self-interstitial atoms (SIAs), as the collision cascades, more Frenkel pairs will be generated (Wilson et al., 1989; Was, 2016). After the displacement phase of the cascade development, the lattice will start to relax, leading to the spontaneous formation of SIA clusters and vacancy

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**Fig. 4.** Elimination of nanoscale features during *in situ* heating. **a–c:** Were conventional TEM images taken at room temperature, before the heating process: **a:** An interface of “clean” and “damaged” area. The “damaged” area has not been sufficiently cleaned by low energy Ar ion milling due to the rocking angle limit of the stage. **b:** Zoomed-in view of the “clean” area, no obvious nanoscale features can be observed. **c:** Zoomed-in view of the “damaged” area, large number density of orthogonal nanoscale features can be observed. **d–f:** Are conventional TEM images of the same region of interest as (a–c), but at 220°C, after heating: **d:** An interface of “clean” and “damaged” area after heating. No obvious nanoscale features can be observed it either the “clean” or the “damaged” area. **e:** Zoomed-in view of the “clean” area after heating, no obvious nanoscale features can be observed. **f:** Zoomed-in view of the “damaged” area after heating, all previously observed nanoscale features were eliminated.

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**Fig. 5.** Scanning Transmission Electron Microscopy of ingot PbTe specimen prepared by ion milling. **a:** STEM BF and **b** STEM HAADF low magnification images simultaneously obtained at the same region of interest. **a:** Depicts large number density of orthogonal nanoscale features while **b** shows very minimal contrast. **c:** STM BF and **d** STEM HAADF high magnification image simultaneously obtained at the same region of interest. **c:** Depicts orthogonal nanoscale features while **d** shows large number density, homogeneously distributed dark clusters. **e:** STEM BF and **f** STEM HAADF high-resolution images obtained simultaneously at the same region of interest. Self-interstitial clusters can be observed (indicated by red arrows).
clusters, as well as the recombination of Frenkel pair defects (Averback, 1982). L. Palmetshofer et al., have reported that ion implantation can generate defect clusters in PbTe and Pb$_{1-x}$Sn$_x$Te (Palmetshofer et al., 1977; Gresslehner & Palmetshofer, 1980; Palmetshofer, 1984).

Fascinatingly, aberration corrected STEM and first principles calculations both suggest that the orthogonal nanoscale features observed in ion milled PbTe specimen should be defect clusters as a result of the ion irradiation during specimen preparation. Aberration corrected STEM was performed on ingot PbTe TEM specimen prepared by ion milling method. Figure 5a is a low magnification STEM BF image of this specimen. A large number density of orthogonal nanoscale features can be observed in this image, which has also been observed in the conventional TEM images taken from other ion milled ingot PbTe specimens. On the other hand, in the HAADF image (Fig. 5b) taken simultaneously at the exact same region of interest, very minimal contrast can be observed. This suggests that the orthogonal nanoscale features are associated with the strong local strain field, but do not have too much Z-contrast compared to the PbTe matrix. Figures 5c and 5d are high magnification STEM BF and STEM HAADF images of the same specimen. While the orthogonal nanoscale features can still be observed in the STEM BF image, homogeneous, randomly distributed dark clusters can be observed in the STEM HAADF image. The dark contrast of the clusters indicates that they have a lower average atomic number than the matrix. Therefore, it is reasonable to attribute these clusters as vacancy clusters randomly distributed in the material. Figures 5e and 5f are high-resolution STEM BF and HAADF images taken at the core of the orthogonal nanoscale features. An
additional set of atom columns were observed in both Figures 5e and 5f, indicated by the red arrows. These additional sets of atom columns demonstrated that these orthogonal nanoscale features are actually SIA clusters parallel to the <001> orientation.

First principles calculations were conducted to answer three important questions: (1) Existing form: Will Frenkel defects prefer to stay as individual defects or defect clusters? (2) Orientation: Why are interstitial clusters observed in STEM BF while conventional TEM images have the orthogonal orientation preference along <001> direction? (3) Species: Are the SIA clusters observed Pb clusters or Te clusters? To answer these questions, formation energies of point defects with different configuration and orientation were calculated. Since practically, the matrix material, PbTe, will not have a strict 1:1 stoichiometric ratio, we calculated defect formation energies in both Pb rich and Te rich environments, shown as the left and right column of Figure 6.

To answer the first question, we calculated the formation energy (per atomic defect) for both the Pb vacancy and Pb SIA in the form of mono-defect, di-defect and tri-defect clusters in both Pb rich and Te rich environments, shown in Figures 6a and 6b. The reason we calculated the formation energy for both Pb rich and Te rich environment is because, in practice, the matrix PbTe material will not have a strict 1:1 stoichiometric ratio. The formation energy per defect decreases as the number of defects in the cluster increases. A similar trend was obtained for the Te vacancy and Te SIA as well, shown in Supplementary Figures S3(a) and S3(b). The fact that defect clusters have lower formation energy gave us a clear answer to the first question: Frenkel defects tend to form defect clusters. As we discussed in Figures 5e and 5f, SIA clusters were observed along <001> orien-
tation. In order to understand this orientation preference, we also calculated formation energy of individual Pb SIA or Pb SIA clusters along the <001>, <011>, and <111> crystal orientations, in both Pb rich and Te rich environments, shown in Figures 6c and 6d, respectively. The theoretical calculation suggests that Pb SIA clusters have the lowest energy along the <001> orientation compared to the <011> and <111> orientations. Similar trends were observed for Te SIA and SIA clusters as well, as shown in Supplementary Figures S3(c) and S3(d). This agrees with the observation in conventional TEM images and STEM HAADF and BF images that SIA clusters locate along the <001> orientation.

The remaining question now is, what type of Frenkel pairs (Pb or Te) were generated to form these vacancy and SIA clusters? We calculated the total formation energy for tri-vacancy and tri-SIA clusters for both Pb and Te in both Pb rich and Te rich environments, as shown in Figures 6e and 6f. It turns out in either the Pb rich or Te rich case, the Pb vacancy-SIA pair has lower total formation energy. We attribute that the species for the SIA cluster observed in S/TEM images are Pb SIA clusters.

**Improvement on TEM Specimen Preparation**

For materials that are potentially multi-phased, ion milling will still be the TEM specimen preparation method to generate considerable size of electron transparent area for structural and chemical analysis. To minimize the misinterpretation of a material’s intrinsic structure due to specimen preparation induced artifacts, extra attention needs to be taken in ion milling conditions. High energy (~1 keV) ion beam can be used at the initial stage until a hole formation to accelerate the specimen preparation process. After that, low energy (~300 eV) Ar ion milling needs to be performed for an extensive amount of time to thoroughly remove the surface damage layer. The entire ion milling procedure should be performed at cryogenic temperature in order to minimize the damage. Since it is observed that the nanoscale features can be eliminated when heated at elevated temperature in TEM, we suggest that appropriate vacuum annealing can also be a potential method to recover the surface damage on lead chalcogenides.

**Summary and Conclusions**

In this work, we identified large number density orthogonal, dark line segment microstructure features along the <001> orientation in ingot PbTe and PbS TEM specimens prepared with ion milling and FIB thinning. With the help of aberration corrected STEM and first principles calculations, these microstructure features are likely to be self-interstitial atom clusters and/or vacancy clusters induced by ion beam irradiation. With low energy Ar ion milling, these features can be significantly reduced or further annihilated upon annealing at high temperature. Understanding the intrinsic microstructure is very essential to correctly attribute the interesting properties and performances of metal chalcogenide materials. TEM specimen preparation needs to be performed cautiously in order to maintain a material’s real microstructure and to avoid artifacts.

**Supplementary material.** The supplementary material for this article can be found at https://doi.org/10.1017/S1431927619000503.

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