Element-resolved atomic structure imaging of rocksalt Ge$_2$Sb$_2$Te$_5$

phase-change material

Bin Zhang, Wei Zhang, Zhenju Shen, Yongjin Chen, Jixue Li, Shengbai Zhang, Ze Zhang, Matthias Wuttig, Riccardo Mazzarello, Evan Ma, and Xiaodong Han

1Institute of Microstructure and Property of Advanced Materials, Beijing University of Technology, Beijing 100124, China
2Center for Advancing Materials Performance from the Nanoscale, State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, Xi’an 710049, China
3I. Institute of Physics (IA), RWTH Aachen University, 52056 Aachen, Germany
4Institute for Theoretical Solid-State Physics, RWTH Aachen University, 52056 Aachen, Germany
5Department of Materials Science and Engineering, Center of Electron Microscopy and State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China
6Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, Troy, New York 12180, USA
7State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun 130012, China
8Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland 21218, USA

(Received 17 March 2016; accepted 25 April 2016; published online 9 May 2016)

Disorder-induced electron localization and metal-insulator transitions (MITs) have been a very active research field starting from the seminal paper by Anderson half a century ago. However, pure Anderson insulators are very difficult to identify due to ubiquitous electron-correlation effects. Recently, an MIT has been observed in electrical transport measurements on the crystalline state of phase-change GeSbTe compounds, which appears to be exclusively disorder driven. Subsequent density functional theory simulations have identified vacancy disorder to localize electrons at the Fermi level. Here, we report a direct atomic scale chemical identification experiment on the rocksalt structure obtained upon crystallization of amorphous Ge$_2$Sb$_2$Te$_5$. Our results confirm the two-sublattice structure resolving the distribution of chemical species and demonstrate the existence of atomic disorder on the Ge/Sb/vacancy sublattice. Moreover, we identify a gradual vacancy ordering process upon further annealing. These findings not only provide a structural underpinning of the observed Anderson localization but also have implications for the development of novel multi-level data storage within the crystalline phases. Published by AIP Publishing.

[http://dx.doi.org/10.1063/1.4949011]

For many years, doped semiconductors have served as the primary systems for the studies of disorder-induced phenomena. However, due to the entanglement with electron-correlation effects, it is difficult to single out the effects of disorder unambiguously. Ge-Sb-Te compounds along the GeTe-Sb$_2$Te$_3$ pseudobinary line, e.g., Ge$_2$Sb$_2$Te$_5$, Ge$_2$Sb$_2$Te$_4$, known as phase-change materials, have been widely used for non-volatile optical and electronic data storage and memory applications. Interestingly, these crystalline compounds also provide an excellent platform to investigate disorder effects, and compelling evidences on exclusive disorder-driven electron localization and metal-insulator transition (MIT) have been reported by electrical transport measurements and density functional theory (DFT) simulations. On the one hand, crystalline Ge-Sb-Te compounds have high dielectric constants due to the resonance between the directional p bonds and thus very weak electron-correlation effects. On the other hand, a significant amount of disorder is reported to exist in these compounds: according to the model by Yamada and Matsunaga, upon rapid crystallization from the amorphous state, a peculiar rocksalt structure (Fig. 1(a)) forms with one sublattice taken by Te, while the other sublattice is randomly occupied by Ge, Sb, and vacancy (e.g., 40% Ge, 40% Sb, and 20% vacancy for Ge$_2$Sb$_2$Te$_5$). In this letter, we experimentally pin down the atomic-level structure and chemistry of this technologically important rocksalt phase and elucidate the existence and the evolution of disorder, employing a state-of-the-art element-resolved atomic imaging method.

The ~20 nm-thick Ge-Sb-Te films were deposited with magnetron sputtering technique on the TEM grids that were covered by an ultrathin (~5 nm) amorphous carbon film, using a stoichiometric Ge$_2$Sb$_2$Te$_5$ alloy target. We use GST as the abbreviation of Ge$_2$Sb$_2$Te$_5$ in the following discussions. First, the samples were annealed in vacuum at various temperatures from 150°C to 180°C for 2 and 30 min. The spherical aberration corrected (Cs-corrected) high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and the energy-dispersive X-ray (EDX) mapping experiments were performed using FEI Titan Cs-corrected ChemiSTEM microscope equipped with a Super-X detector. STEM-HAADF imaging experiments were performed at 200 kV. EDX mapping was obtained at 80 or...
The amorphous GST was found to crystallize into a poly-crystalline cubic (rocksalt) state at 150°C, with grain sizes of 10–20 nm (see also Fig. S1 after annealing at a higher temperature). The HAADF-STEM images display the relative positions of the alternating (111) planes are seen in a periodic pattern, as partially supported by the random-lattices, one indeed exclusively made of Te (Fig. 2(d)) and the other composed of Ge and Sb (Figs. 2(b) and 2(c)). The relative positions of the alternating (111) planes are seen in the composite image in Figure 2(e): the two sublattices together establish the rocksalt crystal. The Ge/Sb maps also reveal that the distributions of Ge and Sb on the cation sublattice are random instead of layer-ordered.

The next task is to demonstrate the existence of intrinsic vacancies on the cation sublattice, which was predicted to be present once such rocksalt structure forms, in DFT simulations and quantum chemistry bonding analysis. The reduced brightness of the spot in the HAADF images can be due to either the presence of atomic vacancies or a higher-than-average concentration of (the lower-Z) Ge. In Figure 2(a), four dimmer spots are highlighted by dotted and solid cyan circles. The atomic column circled by the solid cyan circle (top right corner) is largely due to enriched Ge, as revealed by Figure 2(b). Nonetheless, the three dotted circled cases must be due to excess vacancies, as both Sb and Ge are deficient (in Figs. 2(b) and 2(c)).

Next, we discuss the distribution of vacancies in more detail, as this is highly important to the electronic structure of the crystal. Vacancies seem to distribute randomly rather than in a periodic pattern, as partially supported by the randomness observed from EDX mappings along other crystallographic axes, e.g., the [211] direction (see Fig. S3). Along the [111] direction, we observe that the three vacancy-enriched atomic columns in Figs. 2(a)–2(d) are next to each other. In addition to the statistical fluctuation, this could be due to some vacancies starting to order locally (see discussions on...
the ordering process later), as the sample was kept for 30 min at 150°C. But such vacancy connections are not always the case in other parts of the sample: this is shown in Figures 2(e)–2(k) (and Figs. S3(i)–S3(l)) where the vacancy distribution appears to be more random. Also, in the sample annealed for 2 min at this temperature (Figs. 3(a)–3(c)), such connected dark spots are not found. Therefore, in the early stage after recrystallization from the amorphous phase, atomic vacancies distribute randomly, i.e., in a mostly disordered manner, on the cation lattice of the crystal; the concentration of vacancies fluctuates locally, as seen in Figures 2 and S3. According to the DFT electronic structure simulations (see Ref. 13 and Fig. S4), as long as there are some quasi-spherical vacancy-enriched local regions, e.g., a few Te having 2–4 vacant neighbors, they can result in localization of electronic wavefunctions at the Fermi level, leading to insulating behavior of the sample. We note that our observed crystalline state compares well with the recrystallized models in previous density functional molecular dynamics (DFMD) simulations24,25 in which the vacancies distribute randomly.
on the cation rocksalt sublattice, and hence, should be equivalent to the one obtained by nanoseconds crystallization at high temperature, e.g., 600–700 K.

Upon further thermal annealing, the atomic vacancies are found to segregate onto specific (111) planes, in line with DFT predictions.13,26 The atomic process is shown in Figure S5(a), where a vacant site is occupied by a nearby Ge or Sb atom from the adjacent cation layer. According to our DFT simulations, shown in Fig. S5(b), such migration process leads to an energy gain and the energy barrier is estimated to be around 0.8–1.0 eV, slightly smaller than that reported in crystalline GeTe.26 In addition, vacancy-Te migration is shown to result in an energy loss due to the unfavorable Te-Te antibonds and thus is not expected to take place upon thermal annealing. Evidence of this vacancy ordering process is obtained from our STEM-HAADF experiments on the samples annealed at 160°C and 180°C for 30 min. In Figures 3(d)–3(i), some short and long darker “lines” are observed, which are projections of possible vacancy patches on (111) planes. These ordered vacancy patches increase in number and size, with increasing annealing temperature (Figs. 3, S6, and S7). We note that the mapping region of STEM-EDX is typically too small to capture the formation of dark and long patches; here, we develop a color scheme for the STEM-HAADF images to better visualize the gradual ordering process on the cation sublattice, see Figures 3(c), 3(f), and 3(i). The average value of brightness is set to 1.0 (green), while the darker and brighter values vary from 0.6 (blue-white) to 1.4 (red-yellow), roughly representing the vacancy-rich to vacancy-poor atomic columns. A trend that emerges is that upon further annealing, vacancy-enriched columns (e.g., blue colored columns) increasingly line up together to become more and more plane-like. See further details of the color scheme in Figure S8.

Despite that in some parts of the sample, such vacancy patches are obvious when annealed at 180°C, the sample would still display the insulating behavior in transport measurements,11 as the overall degree of disorder would still be sufficient to induce electron localization. For instance, in Figure S4 we show a DFT model where 50% of certain (111) planes are filled with vacancies, and yet the order developed is still inadequate to eliminate electron localization. We note that this model does not correspond to the samples annealed at 160°C and 180°C for 30 min; it only illustrates the fact that partial vacancy ordering does not imply metallic behavior. In a recent STEM-HAADF work on metastable rocksalt Ge2Sb2Te5,27 highly textured patterns with many regular dark patches from the [110] view were observed; we note that such observation involves extensive vacancy ordering within the crystal, as their samples were annealed at 200°C. This is thus a scenario characteristic of far more extensive annealing, well beyond that of crystallization from the amorphous phase discussed here. The same group also reported a vacancy ordering process under focused electron beam,28 similar to our thermal treatment here. We note that for our measurements, the exposure to electron beam is unavoidable, but there is no obvious vacancy ordering within the limited data collection time, see Figure S9.

At even higher annealing temperatures, 250–350°C, the vacancy ordering process reaches a level that is sufficient to trigger the structural transition to the pseudo-hexagonal phase (with regularly spaced vacancy planes and a different local atomic stacking sequence) and eventually an electronic transition to a delocalized state.11,13 A thorough STEM study of this ensuing structural transition will be our future subject. Previous DFT simulations suggest that an ordered rocksalt phase with regular vacancy planes is significantly lower in energy29,30 and is unstable to induce electron localization, thus it is predicted to display metallic behavior.13 Such ordered cubic phase was produced experimentally and was shown to be metallic.31,32

By tailoring the degree of disorder in GST crystals with thermal treatments, several distinguishable resistance states can be realized. This opens an avenue for binary and multi-level data storage applications within the crystalline phases. A roadblock seems to be the long time required for the vacancy ordering to evolve to various degrees: at low annealing temperatures, it would take minutes for the slow vacancy migration to induce adequate ordering for appreciable change in electrical resistance. However, our DFMD simulations indicate that vacancies can migrate rather rapidly at 500°C (well below the melting temperature 620°C (Ref. 33)); Figure S10 shows that several cation atoms exchanged their positions with vacancies in the adjacent cation (111) layers within a time period as short as 50 ps. At this high annealing temperature, the structural transition to even lower-resistance (pseudo-) hexagonal states (also via vacancy ordering) is expected to occur rapidly as well. Therefore, by carefully engineering the treatment temperature and annealing time, applications for multi-level data storage within crystalline phases may be possible. Such approach could be superior to the traditional multi-level data storage, which functions by tuning the amorphous/crystalline volume ratio within one memory cell,9 in which each resistance state is stable over time, i.e., it suffers much less from resistance drift, which is a known issue of the amorphous phase.9

Before concluding, we mention that the fast crystallization of GST compounds in the phase-change memory applications was argued to be associated with the existence of Ge in tetrahedral sites (GeT).35–38 But GeT in amorphous GST and GeTe was reported recently to disappear upon structural relaxation at room temperature.39 Our STEM-EDX measurements reported here found no obvious GeT in the crystalline GST. Previous TEM measurements40 on crystalline GST showing significant amount of GeT might have been performed on some intermediate state of the sample captured during the crystallization process. Instead, the high fragility of the compounds may be responsible for the fast crystallization ability.33,40,41

In conclusion, we have experimentally studied the sublattice structure of the technologically important crystalline phase of GST, taking advantage of a state-of-the-art element-resolved atomic imaging technique. We have experimentally verified the distribution of chemical species, in particular that of Ge, Sb, and vacancy on the cation sublattice, which is shown to constitute a very significant degree of atomic disorder. This direct observation supports the lattice-disorder-induced electron localization that renders rocksalt GST a typical Anderson insulator. Moreover, our systematic atomic imaging experiments on samples under different annealing
conditions delineate a vacancy ordering process within the crystal, well beyond the stage after fast amorphous-to-crystal transition. All of these findings call for further investigations on the disorder-induced phenomena in phase-change materials and on the design of multi-level data storage devices based on the tailoring of disorder.

We gratefully thank Zhitang Song and Yan Cheng for providing samples that enabled useful comparisons. B.Z., Y.J.C., and X.D.H acknowledge National Key Basic Research Program of China, 2013CBA01900; the Key Project of National Natural Science Foundation of China (11234011); Beijing High-level Talents (PHR20100503), the Beijing PXM2011014204000053 and National/Beijing 211 projects. W.Z. gratefully thanks the Young Talent Support Plan of Xi’an Jiaotong University. R.M. and M.W. acknowledge the computational resources provided by Xi’an Jiaotong University. R.M. and M.W. acknowledge the funding from Deutsche Forschungsgemeinschaft (DFG) within SFB 917 (“Nanoswitches”) as well as ERC Advanced Grant Disorder Control (M.W.). E.M. acknowledges the support from the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Division of Materials Sciences and Engineering, under Contract No. DE-FG02-13ER46056. W.Z. and R.M. also acknowledge the computational resources granted by JARA-HPC from RWTH Aachen University under Project JARA0089 and JARA0114.