

Element-resolved atomic structure imaging of rocksalt Ge₂Sb₂Te₅ phase-change material

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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 Ge₂Sb₂Te₅. Our results confirm the twosublattice 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 multilevel data storage within the crystalline phases. Published by AIP Publishing.

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For many years, doped semiconductors^{1,2} have served as the primary systems for the studies of disorder-induced phenomena.^{3,4} However, due to the entanglement with electron-correlation effects,⁵ it is difficult to single out the effects of disorder unambiguously. Ge-Sb-Te compounds along the GeTe-Sb₂Te₃ pseudobinary line,⁶ e.g., Ge₂Sb₂Te₅, Ge₁Sb₂Te₄, known as phase-change materials, have been widely used for non-volatile optical and electronic data stor-age and memory applications.^{7–10} Interestingly, these crystalline compounds also provide an excellent platform to investigate disorder effects, and compelling evidences on exclusive disorder-driven electron localization and metalinsulator transition (MIT) have been reported by electrical transport measurements^{11,12} and density functional theory (DFT) simulations.^{13,14} On the one hand, crystalline Ge-Sb-Te compounds have high dielectric constants due to the resonance between the directional p bonds^{15,16} 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,^{6,17} 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 $Ge_2Sb_2Te_5$). 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 elementresolved atomic imaging method.

The \sim 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 Ge₂Sb₂Te₅ alloy target. We use GST as the abbreviation of Ge₂Sb₂Te₅ in the following discussions. Then 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 Cscorrected ChemiSTEM microscope equipped with a Super-X detector. STEM-HAADF imaging experiments were performed at 200 kV. EDX mapping was obtained at 80 or

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FIG. 1. Atomistic models and STEM-HAADF images of rocksalt GST. (a) The classic rocksalt model with Te (green spheres), Ge (red spheres), Sb (blue spheres), and vacancy (grey circles). (b) The atomic arrangements along the [001], [111], [110], and [211] crystallographic orientations. In the [001] and [111] views, each column is comprised of four ingredients, Te/Ge/Sb/Vac (gold spheres). In the [110] and [211] views, one set of atomic sites is taken by Te (green spheres), while the other one is taken by Ge/Sb/Vac (pink spheres). HAADF images along four crystallographic axes: (c) [001], (d) [111], (e) [110], and (f) [211]. In the bottom right corner of each panel, possible atomic arrangements are depicted.

200 kV. See the supplementary material for more experimental details.¹⁸ Such imaging method has been shown to be powerful in identifying the atomic structure and defects on very relevant compounds, such as Bi_2Te_3 , and doped Sb_2Te_3 .^{19,20} We note that our samples were produced and thermally annealed under the same conditions as those reported in Ref. 11; therefore, the electrical transport properties of our samples are expected to be the same as in Ref. 11.

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 actual positions of atoms, in the form of projections of atomic arrangements along different directions, as displayed in Figure 1. These HAADF images were taken along the [001], [111], [110], and [211] directions, and from which the spacings of (002) and (220) planes are measured as ~3.0 Å and ~2.1 Å, respectively, which are in agreement with previous X-ray diffraction data.¹⁷ The brightness of each spot is roughly proportional to Z² (Ref. 21), where Z represents the

average atomic number (here, Ge 32, Sb 51, Te 52, vacancy 0) of the atomic column. In Figures 1(c) and 1(d), the brightness of the spots appears to be rather uniform, because in the [001] and [111] directions each atomic column is constituted of all the four ingredients (Ge/Sb/Te/vacancy) (see Fig. 1(b)), resulting in a similar averaged Z value. In contrast, imaging along the [110] or [211] directions should distinguish the two sublattices of the rocksalt structure (see Fig. 1(b)). This is indeed what is observed in the HAADF images shown in Figures 1(e) and 1(f): one sublattice exhibits uniformly bright spots, suggesting that it is solely occupied by the heavier species, Te. On the other sublattice, the spots are obviously darker and display varying brightness, suggesting the occupation of Ge, Sb, and vacancy in random proportions for each column. The superposition of the two sublattices produces the alternating brightness as shown with an intensity line scan in Figure S2(b).

However, the brightness and its contrast in HAADF images could have multiple origins, as we have three different elements and possible vacancies. A direct observation of elemental distributions at the atomic level is therefore essential in order to reach our goal of unequivocally pinning down the structure/chemistry in Figure 1(a) and being able to monitor the ordering of vacancies. This motivated us to carry out atomic scale EDX chemical mapping experiments. The data were collected from the same sample (annealed at 150 °C for 30 min). In Figures 2(a) and 2(f), we present two [110] HAADF images together with corresponding chemical mappings for Te (green), Ge (red), and Sb (blue) (Figs 2(b)-2(d) and 2(g)-2(i)). All atoms are generally localized on their atomic sites, and there are indeed two clearly distinguishable sublattices, 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 rather random instead of layer-ordered.²²

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.²³ 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



FIG. 2. Structural and chemical identifications of rocksalt GST along the [110] direction. (a)–(e) The HAADF image, the respective EDX chemical mapping for individual Ge (red), Sb (blue), and Te (green), and overlaid chemical map showing the relative positions of two sublattices. Vacancy-enriched atomic columns are marked with dotted cyan circles, while a Ge-enriched atomic column is marked with solid cyan circle. (f)–(j) Taken from another part of the same sample: vacancy-enriched atomic columns are not obvious.

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) simulations^{24,25} in which the vacancies distribute randomly



FIG. 3. Vacancy ordering in rocksalt GST after annealing at different temperatures. (a)-(c) The sample annealed at 150°C for 2 min, (d)-(f) 160°C, and (g)-(i) 180°C for 30 min. The HAADF images were acquired along the [110] direction. Boxed regions in (a), (d), (g) are magnified in (b), (e), (h) and the corresponding normalization maps for cation sublattice are shown in (c), (f), and (i). The color bar represents the relative intensity derived from the spot brightness in HAADF images. The average value is set to be 1.0 (green), while the darker and brighter spots vary from 0.6 (bluewhite) to 1.4 (red-yellow), roughly representing vacancy-rich to vacancypoor atomic columns.

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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 energy^{29,30} 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 multilevel 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 $620 \,^{\circ}\text{C}$ (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 states³⁴ (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 (Ge^T).^{35–38} But Ge^T 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 Ge^T in the crystalline GST. Previous TEM measurements³⁶ on crystalline GST showing significant amount of Ge^T 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 elementresolved 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-disorderinduced 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.

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