The impact of vacancies on the stability of cubic phases in Sb–Te binary compounds

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Abstract
Data retention ability and number of cycles are key properties of phase change materials in applications. Combining in situ heating transmission electron microscopy with ab initio calculations, we investigated the phase transitions of binary Sb–Te compounds. The calculations indicated that the vacancies in Te sites destroyed the framework of the cubic phase, which agrees well with the absence of cubic phases observed during in situ heating experiments when the Sb concentration exceeded 50%. In contrast, the vacancies in Sb sites stabilized the cubic structure. Further analysis of the charge density maps revealed that the distribution of antibonding electrons may be the origin of the driving force for structural transitions. Furthermore, our results also showed that reducing the vacancies greatly increased the phase transition temperatures of both the amorphous-cubic and cubic-trigonal phases and therefore may improve the data retention ability and cyclability of phase change materials. This result also implies that doping Sb–Te compounds may provide an approach to discover novel phase change materials by reducing the amount of vacancies.

Introduction
Recent major breakthroughs that addressed the limitations1 of phase change memory (PCM) are renewing interest in it as a promising next-generation technology for electronic data storage and computation2,3. If the performance of PCM could compete with that of dynamic random access memory (DRAM), completely new computer architectures would be enabled5. To date, the most widely studied systems lie on, or are in the vicinity of, a pseudobinary line that joins the stoichiometric compounds Sb2Te3 and GeTe. Among these compounds, the alloy Ge2Sb2Te5 has the best combination of properties: fast crystallization, amorphous phase stability, high endurance limit and excellent contrast;6 therefore, it has attracted the largest amount of attention. The crystalline phase utilized in GeSbTe-based PCMs that are currently in use is the cubic metastable phase, which contains large quantities of vacancies6–8. The vacancies in the Ge/Sb sublattice are intrinsic9 and have been demonstrated to play an important role in phase transitions and related properties10–17.

Replacing DRAM with PCM is a formidable challenge because of the combined requirements of a fast switching speed and extremely high cycle numbers. Although a Sb-rich GeSbTe PCM demonstrated 1011 cycles under accelerated testing conditions18, the required cycle numbers for a DRAM replacement have not been achieved4. One of the main failure mechanisms of PCM devices is void formation over the bottom electrode contact. The other main failure mechanism is elemental segregation, which leads to poor data retention when the cell can no longer be switched to the high-resistance state or does not remain in the high-resistance state since Sb-rich alloys have low crystallization temperatures4.

In terms of the failure mechanism in GeSbTe-based PCMs, Sb–Te alloys have advantages compared to GeSbTe alloys, e.g., a simple composition, which prevents the phase separation that occurs in GeSbTe alloys. As the parent material of GeSbTe PCMs, Sb2Te3 and its promise
have been ignored for a substantial amount of time. Recently, Zheng et al. proved that the metastable face-centered cubic (FCC) \( \text{Sb}_2\text{Te}_3 \) phase does exist\(^8\). A series of studies showed that doped \( \text{Sb}_2\text{Te}_3 \) exhibits excellent properties that are required for PCMs\(^19\)\(^20\), such as a fast phase transition speed, good reversibility at elevated temperatures and good thermal stability at room temperature. In 2017, Rao et al. demonstrated that the \( \text{Sb}_{0.2}\text{Sb}_2\text{Te}_3 \) compound that they designed achieved a writing speed of only 700 picoseconds\(^7\). The ultrafast crystallization is due to the reduced stochasticity of nucleation through geometrically matched and robust scandium telluride (ScTe) chemical bonds that stabilize the crystal precursors in the amorphous state. This makes \( \text{Sb}_2\text{Te}_3 \) an attractive competitor to DRAM because of the ultrafast writing speed. Unfortunately, as a DRAM replacement, \( \text{Sb}_2\text{Te}_3 \) possesses the same shortcomings as \( \text{GeSbTe} \). Due to the large quantities of volatile vacancies in the metastable phase, the cubic phase has a strong tendency to transform into a stable trigonal phase during cyclic writing processes. The vacancy ordering and evaporation from the cubic phase to the trigonal phase result in a density change\(^21\), which causes void formation, triggering the failure of PCMs\(^4\). Additionally, pure \( \text{Sb}_2\text{Te}_3 \) has a very low crystallization temperature and thus a poor data retention ability.

Here, in this work, we systematically investigated the phase transitions of \( \text{Sb–Te} \) binary compounds between \( \text{Sb}_2\text{Te}_3 \) and \( \text{Sb}_2\text{Te} \) by combining in situ heating transmission electron microscopy (TEM) and ab initio calculations. The in situ TEM experiments showed that vacancies play a central role in the phase transition temperatures of \( \text{Sb–Te} \) compounds. The ab initio calculations revealed that the vacancy type is the factor that determines the existence of a cubic phase and that the amount of vacancies has a great impact on the phase transition temperatures.

**Materials and methods**

**Film preparation and characterization**

The TEM samples (~15 nm) were deposited on copper grids with an ultrathin carbon support by varying the RF sputtering power on \( \text{Sb} \) and \( \text{Sb}_2\text{Te}_3 \) targets by physical vapor deposition (PVD). The deposition rate was measured from cross-section samples by scanning electron microscopy (SEM). The sample composition was tested by energy dispersive spectroscopy (EDS) (shown in Supplementary Fig. 10). The in situ heating experiments were performed with TEM (JEOL 2100F) with a heating rate of 10 °C/min using a single tilt holder (Gatan 628). To alleviate the influence of electron irradiation, the samples were exposed to the beam for a short time at the capturing temperature, and the area was changed for each observation. High-resolution TEM (HRTEM) experiments were performed on a JEOL-ARM300F instrument with a double Cs corrector operating at 300 kV.

**Ab initio theoretical simulation**

The ab initio calculations were carried out by employing the Vienna ab initio simulation package (VASP)\(^22\) with projected augmented wave (PAW) pseudopotentials\(^23\) and Perdew-Burke-Ernzerhof (PBE) functionals\(^24\). The 14.942 × 14.942 × 31.697 (Å) supercell of the FCC structure was built. For the stable structures with a trigonal phase with van der Waals (vdW) gaps, the DFT-D2 method of the Grimme scheme\(^25\) was used for corrections. The energy cut-off was set to 235 eV, and the \( \Gamma \) point was used in the Brillouin zone sum. Chemical bonding analysis was carried out by combining a charge density map with the COHP method\(^26\). The Local Orbital Basis Suite Towards Electronic-Structure Reconstruction (LOBSTER) code\(^27\) handles the DFT calculation results and projects them onto localized atomic basis sets\(^28\). The activation energies of the atom/vacancy diffusion were calculated using the nudged elastic band (NEB) method\(^29\)\(^30\).

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**Fig. 1** The electron diffraction profiles showing the structure evolutions of Sb-Te binary compounds in in-situ TEM heating experiments. a Intensity profiles extracted from diffraction rings at an elevated temperature for different Sb concentrations. b The temperature of the different phase changes with the variation in the Sb concentration. Blue represents the amorphous phase (A), green represents the FCC phase (F) and red represents the trigonal phase (T).
**Results and discussion**

In situ TEM characterization of the phase transformations of Sb–Te compounds

Figure 1a shows an intensity profile extracted from the diffraction patterns (Supplementary Figs 1–4) of in situ heating experiments for Sb–Te compounds with different Sb concentrations. In Fig. 1a, the intensity profiles of the diffraction patterns indicate that partial Sb₂Te₃ films crystallized even at room temperature. Some crystalline grains (below 10 nm) were found in the TEM bright-field (BF) image (Supplementary Fig. 1). The indexed diffraction pattern shows that the structure at room temperature belonged to the FCC phase. With increasing temperature, an increasing number of large grains (~10 nm) appeared. The intensity profiles of the diffraction patterns indicated that up to 120 °C, the crystals retained the cubic structure. At 140 °C, the 2θ value of the (200) FCC peak decreased, indicating that the phase changed to a trigonal structure.

When the composition approached SbTe (Sb₄₈Te₅₂), the intensity profile of the as-deposited film was characterized as an amorphous phase. Although some grain-like particles appeared in the BF image at 100 °C (Supplementary Fig. 2), the cubic phase did not appear in the intensity profile until 120 °C and remained until 200 °C. At 200 °C, the (222) peak of the cubic phase shifted slightly to the left, indicating incubation of the trigonal

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**Fig. 2** FCC models with different types and amounts of vacancies. a Relaxed structures. b The corresponding formation energies (Eₐ)
phase. When the temperature increased to 220 °C, the intensity profile showed a well-characterized trigonal phase. To confirm the structure of the Sb$_{48}$Te$_{52}$, HRTEM was performed to observe the image of the film after heating to 160 °C (Supplementary Fig. 5). The HRTEM images of the $<001>$, $<111>$ and $<110>$ zone axes clearly indicate the existence of the FCC phase, which is quite similar to cubic Sb$_2$Te$_3$. However, when the composition crossed the SbTe line, the phase transition of the compound abruptly changed. As shown in Fig. 1a, the intensity profile indicates that the cubic phase in the above compounds disappeared in the Sb$_{52}$Te$_{48}$ compound. Partial Sb$_{52}$Te$_{48}$ began to directly crystallize to the trigonal phase at 120 °C (Supplementary Fig. 3). With increasing temperature, additional crystalline diffraction spots appeared. Up to 160 °C, the compound completely crystallized to the trigonal phase. In comparison, when the composition of the Sb–Te compound approached Sb$_2$Te, all the compounds quickly crystallized into the trigonal phase at 140 °C (Supplementary Fig. 4).

According to the results of the in situ heating experiments, the phase transition temperatures vs various Sb concentrations are summarized in Fig. 1b. As shown in the figure, a distinct boundary appeared when the Sb concentration equaled 50%. When the Sb concentration was greater than 50%, the cubic phase was not observed. The cubic phase was only obtained when the Sb concentration was lower than 50%. In addition, the data reveal that the phase transition temperatures of both the amorphous-cubic and cubic-trigonal phases increased with increasing Sb concentration or decreasing amount of vacancies of the Sb sites in the cubic Sb–Te compounds.

**Ab initio calculations revealing the stability of FCC Sb–Te structures with different types and amounts of vacancies**

To understand the in situ heating TEM experimental results, we performed ab initio calculations. For a comparison with the trigonal phase, a hexagonal supercell with P1 symmetry was designed according to the FCC structure, with 108 Sb atoms on one sublattice and 108 Te atoms on the other sublattice. Based on this structure, Sb and Te atoms were removed randomly to create vacancies, and then the structures were relaxed to their ground state energy. By removing 36 Sb atoms, the composition of the supercell was the same as Sb$_2$Te$_3$. By removing 54 Te atoms, the composition of the supercell was the same as Sb$_2$Te.

As presented by the atomic models in Fig. 2a, the structural frameworks of the cubic phase remained well defined after removing the Sb atoms, even when the number of atoms removed reached 36. In contrast, the removal of 18 Te atoms severely deformed the local structures. After removing 36 Te atoms, the framework of the cubic structure was completely destroyed, and the situation deteriorated after removing 54 Te atoms. In addition, the corresponding formation energy ($E_f$) was also calculated to reveal the stability of the cubic structures.

As depicted in Fig. 2b, the cubic structure with Sb vacancies had a negative $E_f$. The value of $E_f$ was the lowest...
when the composition approached Sb$_{72}$Te$_{108}$ (namely, Sb$_2$Te$_3$), and $E_f$ gradually increased to zero as the Sb concentration approached 50%. The low value of $E_f$ means that Sb$_2$Te$_3$ was more energetically favorable. This explains why the as-deposited Sb$_2$Te$_3$ crystallized at room temperature. When the Sb concentration was above 50%, $E_f$ increased above zero except for in Sb$_{108}$Te$_{90}$. Even with a negative formation energy, the cubic structure was impossible because of the severe deformation of the structural framework, as shown in Fig. 2a.

**Charge density maps revealing the electronic structures of the Sb–Te phase**

To understand what leads to the distinct behaviors of the phase transition for Sb–Te compounds, we revisit the basic electronic structure of Sb and Te atoms, which have s$^2$p$^3$ and s$^2$p$^4$ outer shell structures, respectively. Therefore, the most favorable bonding environments for Sb and Te are 3 and 2 p-bonding coordinated atoms, respectively. Figure 3a and b shows the charge density maps of the stable phases for Sb$_2$Te$_3$ and Sb$_2$Te, respectively.

As shown in the left panel in Fig. 3a, the most stable compound for Sb–Te alloys was the Sb$_2$Te$_3$ trigonal phase, where, on average, Sb has 3 coordinated Te atoms and Te has 2 coordinated Sb atoms. Even for the stable phase, the local coordination environments for Sb and Te were not perfect. Thus, antibonding states still existed in the stable phase (Supplementary Fig. 6, the crystal orbital Hamilton populations (COHPs) of Sb$_2$Te$_3$ and Sb$_2$Te). As shown in the right panel in Fig. 3a, these antibonding states were dominated by electrons surrounding Te. Moreover, in the octahedral bonding environment, Te–Te bonding was not favorable because the coordination environment was contradictory to the preferable requirement, which is the right angle zigzag chain structure$_{31}$. In contrast, Sb–Sb bonding was more energetically preferable than Te–Te bonding because the bonds can be saturated with three perpendicular p-bonds, as shown by the Sb$_2$ lamina in Fig. 3c. For the Sb$_2$Te compound, the most stable structure was constructed by one laminar Sb$_2$Te$_3$ layer plus two extra laminar Sb$_2$ layers (Fig. 3b). These basic facts set up the prerequisites that the alloying structures must obey in the phase transitions.
When Sb and Te were arranged into a theoretical rock-salt (RS) structure, there were 7 electrons in the Sb and Te p-orbitals. This means that the p-orbitals for Sb and Te were overloaded. Thus, the extra electrons in the p-orbitals were forced into the antibonding states. In this RS structure, as shown in Fig. 4a, the electrons of the antibonding states (Supplementary Fig. 7a) surrounded both Sb and Te atoms, and the energy of the Sb–Te composite was high. Removing Sb atoms decreased the formation energy of the cubic Sb–Te composites, as shown in Fig. 2b. In contrast, vacancies of the Te sites greatly increased the formation energy of the Sb–Te compounds and destroyed the cubic framework. Figure 4b, c show the charge density maps of the antibonding states for unrelaxed cubic Sb$_{72}$Te$_{108}$ and Sb$_{108}$Te$_{72}$, respectively. As shown in Fig. 4b, after removing 36 Sb atoms, the electrons of the antibonding states were only found around the Te atoms. This is similar to the charge density map of the antibonding states for trigonal Sb$_2$Te$_3$, indicating a decreased formation energy. However, the vacancies of the Te sites resulted in more antibonding electrons (Supplementary Fig. 7b and c). Furthermore, in contrast to Sb$_{72}$Te$_{108}$, the antibonding electrons in Sb$_{108}$Te$_{72}$ mainly surrounded the Sb atoms, suggesting a relatively high formation energy.

Relaxation further deceased the ground state of a structure by finding more suitable atom positions in a cell. As shown in Fig. 4d, the structure of Sb$_{72}$Te$_{108}$ adjusted slightly due to the similarity of the distributions of the antibonding electrons between cubic and trigonal phases. In contrast, the dramatic difference in the distribution of antibonding electrons in the Sb$_{108}$Te$_{72}$ composite resulted in a high driving force for the relaxation of the structure (this can also be seen from the COHP difference before and after the relaxation in Supplementary Fig. 7c and d). This difference collapsed the cubic framework. The charge density map in Fig. 4e shows that the atoms surrounded by antibonding electrons changed to Te from Sb after relaxation. Some Sb–Sb bonds appeared after relaxation (Supplementary Fig. 8). These results agree well with the structure of trigonal Sb$_2$Te.
Vacancies decreasing the diffusion energy barriers

The phase transition temperature from the cubic phase to the trigonal phase was determined by the activation energy ($E_a$) for atom/vacancy diffusion in the cubic framework. The activation of diffusion is required by the vacancy ordering and evaporation in the phase transition. This activation energy is defined by the energy barrier that the atom/vacancy must overcome in the diffusion path. The corresponding phenomenon in GeTe-Sb$_2$Te$_3$ pseudobinary alloys, where more Sb$_2$Te$_3$ means a decreased phase transition temperature$^9$.

The metastable cubic phases in our in situ TEM experiments only appeared when the Sb concentration was lower than 50%. This special composition-dependent phase transition was also demonstrated in thick samples (~100 nm) by resistance-temperature (R-T) measurements (Supplementary Fig. 9).

In summary, in situ heating TEM experiments combined with ab initial calculations were employed to understand the phase transitions in Sb–Te binary compounds. Vacancies were found to have a strong impact on the stability of cubic phases for Sb–Te compounds. The distribution of antibonding electrons supplied the driving force for the structural transitions. Furthermore, the results also showed that reducing the vacancies greatly increased the phase transition temperatures for both amorphous-cubic and cubic-trigonal phases, thus improving the data retention ability and cyclability. Doping may reduce the vacancies of the crystalline phase. Moreover, this also increased the stability of the amorphous phase$^9$, further improving the data retention ability. Doping Sb–Te compounds may provide an approach to discover better phase change materials for DRAM applications.

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Conflict of interest

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