Direct atomic insight into the role of dopants in phase-change materials

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Doping is indispensable to tailor phase-change materials (PCM) in optical and electronic data storage. Very few experimental studies, however, have provided quantitative information on the distribution of dopants on the atomic-scale. Here, we present atom-resolved images of Ag and In dopants in Sb2Te-based (AIST) PCM using electron microscopy and atom-probe tomography. Combining these with DFT calculations and chemical-bonding analysis, we unambiguously determine the dopants’ role upon recrystallization. Composition profiles corroborate the substitution of Sb by In and Ag, and the segregation of excessive Ag into grain boundaries. While In is bonded covalently to neighboring Te, Ag binds ionically. Moreover, In doping accelerates the crystallization and hence operation while Ag doping limits the random diffusion of In atoms and enhances the thermal stability of the amorphous phase.
O
ver the last 50 years, computers have revolutionized almost every aspect of modern life, in particular com-
munication, education, entertainment, and science, too.
Today, however, they face increasing demands for faster data access and larger storage capacity, which are both severely limited by the presently available memory (fast, volatile, small) and stor-
age (slow, non-volatile, large) hierarchies1-2. One successful
approach for technological improvement is the introduction of
phase-change memory3, also marketed by Intel/Micron as 3D
Xpoint4. It takes advantage of the ability to switch the resistance
upon the phase transition from a disordered amorphous (logic 1)
to an ordered crystalline phase (logic 0) in certain chalcogenides,
providing nonvolatility, nanoseconds speed and 4P² (F: feature
size) density5-9, thereby bridging the performance gap between
memory and storage1. The successful commercialization of phase-
change memory has been enabled by successful doping chalco-
genides in the pseudo-binary GeTe-Sb₂Te₃ family7,8, as well as Ag
and In doping Sb₂Te alloy abbreviated as AIST, in which between
3.4 at. % and 11 at. % Ag and In have been incorporated9,10.
Thanks to enhanced erasibility and sensitivity, AIST has been
frequently used in rewritable optical-storage media such as CD-
RW and DVD-RW, already since 19939,10. Moreover, AIST is
frequently used in rewritable optical-storage media such as CD-
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further atom-resolved EDX was used to resolve
elements with similar atomic numbers and low Ag and In
concentrations. Further atom-resolved EDX was used to resolve
Ag and In dopants in AIST, due to limits of analytical technology. This
hinders further material optimizations to boost device perform-
ance, especially with regards to operation speed and device
duration. In the earliest report from 1993, Iwasaki et al. employed
X-ray diffraction (XRD) and transmission electron microscopy
(TEM) and showed that AIST, with 11 at.% Ag and In, crystal-
lized not as a single phase but as a solid mixture of Ag₃Te₂ and
Sb₂ phases after annealing at 230 °C10. They also observed a solid-
state reaction of these phases to yield AgSbTe₂ and InSb as the
temperature increases to 350 °C. In 2001, Matsunaga et al. utilized
synchrotron-radiation XRD and proposed a uniform A7 crystal
structure (R3m) with just one crystallographic site, randomly
occupied by all atoms (Ag, In, Sb, or Te). It subsequently changes
upon annealing to a rhombohedral structure at ~507 °C13. I n
contrast, Raoux et al. discovered that the XRD pattern of AIST
resembled pure Sb₃Te, characterized by the repeated stacking of
Sb₂ bilayers and Sb₂Te₃ quintuple layers14. Based on a statistical
technique called fluctuation TEM, Lee et al. directly detected the
nanometer-scale nuclei embedded in AIST and their evolution
over time15. Later, Matsunaga et al. combined extended X-ray
absorption fine structure (EXAFS), hard X-ray photoelectron
spectroscopy (HXP) and reverse Monte Carlo (RMC) simula-
tions, and determined a distorted octahedral atomic arrange-
ment of Sb and Te atoms but were less successful to explain the
precise role of Ag and In atoms15. In both aforementioned cases,
as well as in the recent density-functional theory (DFT) calcula-
tions16, a randomly mixed structure of AIST was used.
In this contribution, we provide atomic insight of the
distribution of 5.13 at.% Ag and 3.32 at.% In within polycrystalline
thin films of AIST, the composition of which is close to that used
in rewritable optical-storage media such as DVD-RW (~5 at.%
Ag and ~5 at.% In)15. First their occupancy in the main structure of
the grains is revealed by atomically resolved aberration-
corrected scanning TEM (Cs-corrected STEM). In addition,
quantitative information is provided by atom-probe tomography
(APT) performed specifically at grain boundaries. Ultimately,
the structure model obtained is fed into density-functional theory
calculations and analyzed by chemical-bonding theory, through
which the precise role of each element in the recrystallization
process is revealed.

Results
Structure and chemical identifications. Figure 1 presents the
atomic arrangement and element distributions of crystalline AIST
obtained from in situ TEM investigation. The atomically resolved
high-angle annular dark-field (HAADF) images in Fig. 1a show
that crystalline AIST annealed at 200 °C is stacked by both bilayer
and quintuple-layer units. Ag, In, Sb, and Te are distributed
inhomogeneously, with Ag and In showing a preference to the
Sb₂Te₃ quintuple layers, while the bilayers are built from mostly
Sb. After increasing the temperature to 350 °C (Fig. 1b–d), the changes in atomic arrangement are miniscule, while the degree of
crystallinity increases with higher heating temperature, as indi-
cated by clearer atomic energy-dispersive X-ray spectroscopy
(EDX) mappings.
To investigate the influence of annealing time on the atomic
arrangement, the sample was annealed at 300 °C for 30 min, so
Fig. 2 shows additional micrographs after this annealing step.
Appropriately, as seen from the HAADF image in Fig. 2a, crystalline AIST shows a bilayer stacking sequence, separated by narrow
gaps, which is commonly found in crystalline AIST13. The
observed atomic arrangement remains the same as that observed
in Fig. 1, which suggests that the crystalline structure of AIST
is barely affected by the annealing time. Correspondingly, the line
profile taken across four bilayers shows two kinds of atomic
column distances (Supplementary Fig. 1), 2.06 Å and 2.61 Å, in
line with the Matsunaga model (Supplementary Fig. 2)13. The
atomic configuration is identical to that of the rhombohedral
(A7-type) Sb crystal projected along the <001> direction17. A
~20% variation in bond lengths (three shorter and three longer
bonds) is observed, which is attributed to the three-dimensional
energy-lowering Peierls distortion of the ideal rocksalt struc-
ture18. These bilayer structures (marked by yellow boxes) are
replaced in some regions, as shown in Fig. 2a, by quintuple layer
(highlighted by green boxes). Two interplanar distances are
shown in the quintuple layer (Supplementary Fig. 1), namely
2.22 Å and 2.34 Å, slightly larger than those of the interlayer
distances. The quintuple layer is surrounded by bilayers at a
spatial width of 2.48 Å. Thereby, AIST has a crystalline structure
resembling undoped Sb₂Te, characterized by a systematic
stacking of ordered bi- and quintuple-layer blocks (as proposed
by Kifune et al.19), which is significantly different from the
repeated bilayer stacking in the Matsunaga model13. However,
these two building blocks of Sb₂Te are randomly distributed in
crystalline AIST (comparing Fig. 2 and Supplementary Fig. 1),
lacking the distinct order found in the binary compound.

While the intensity of the atoms in HAADF images is
approximately proportional to Z² (ref. 20), suggesting a Te-Sb-
Te-Sb-Te quintuple layer, the figures still lack information
regarding Ag and In. This is attributed to the presence of four
elements with similar atomic numbers and low Ag and In
concentrations. Further atom-resolved EDX was used to resolve
the occupancy, as shown in Fig. 2b to h. Apparently, as seen from
Fig. 2a, two quintuple blocks are separated by five continuously
stacked bilayers. Indeed, the stacking sequence of a quintuple
layer is Te1-Sb-Te2-Sb-Te1, as mentioned above, which can be
observed directly from the Sb, Te and their overlay mappings in
Fig. 2d to f, respectively. Noticeably, as shown in Fig. 2b, c, the
dominantly resolved signals from Ag and In atoms stem from the
same sites within the quintuple layers as the Sb atoms. These
dopants thus substitute Sb, and are hence dubbed Ag₃Sb and In₃Sb,
with the Sb subscript denoting the substitution site. They are
more visualized in the overlaid Ag + Te and In + Te in Fig. 2g, h,
respectively. In contrast, Sb exclusively occupies the bilayers between the Te-Sb-Te-Sb-Te quintuple layers, and no significant amount of Te, Ag, or In can be detected inside the bilayers. As shown in Supplementary Fig. 3, AgSb and InSb defects are dramatically reduced as a defective quintuple-layer splits into bilayer and triple-layer (with a small gap between them), as also observed in the crystalline Ti-Sb-Te alloy. Summarizing, the atomic stacking model of crystalline AIST is schematically presented in Fig. 2i. The layered stacking configuration obviously differs from the randomly mixed model proposed by Matsunaga et al. in 2001.

Element distributions in the grain boundary. Noticeably, Ag atoms not only locate in the Sb$_2$Te$_3$ quintuple layer, forming AgSb defects, but also aggregate in the grain boundary (GB), as shown in the EDX mappings in Supplementary Fig. 4. In contrast, fewer In, Sb and Te atoms are found in the grain boundary, supported by the lower intensity than those inside the grains. To provide quantitative information on the distribution of Ag within both grains and GB, we performed correlative TEM-atom-probe tomography investigations. APT has high elemental sensitivity (>1‰) and provides sub-nanometer-scale mapping in three-dimensions. The principle of APT is illustrated in the method section and highlighted in ref. Figure 3A shows the HAADF-STEM image of the needle-shaped APT specimen. The presence of a high-angle GB is assessed by the different diffraction patterns on either side of the feature highlighted by the red arrow. Figure 3B presents the corresponding reconstructed three-dimensional (3D) mapping obtained from APT. The location of the grain boundary is indicated by the dark orange dashed arrow. A set of iso-surfaces encompassing regions of the point cloud containing over 7.5 at.% Ag and 5.5 at.% In are overlaid onto the point cloud in red and yellow, respectively. The thresholds were adjusted to highlight the non-homogeneous distribution of these elements throughout the microstructure. The one-dimensional composition profile displayed in Fig. 3c was calculated along a $d = 50$ nm cylindrical region-of-interest positioned normal to the grain boundary, as indicated in the inset, in which a top-view of the grain boundary is displayed. The dashed lines correspond to the average composition within the grains. Inside both grains, the composition is 65.5 at.% Sb, 26.6 at.% Te, 3.9 at.% Ag, and 3.3 at.% In. The grain boundary is In-depleted, with a composition dropping to ~2 at.%, which contrasts with a statistically significant segregation of Ag up to 6 at.%. This result is consistent with the EDX mappings in Supplementary Fig. 4. From the grain boundary, a 40 nm-thick region extends into the grain. This layer is slightly enriched in Ag, to ~5 at.%, and in Te at 27 at.%, accompanied by a corresponding depletion of Sb to 63.5 at.% and of In to 2.8 at.%. This means that all In atoms substitute Sb atoms, whereas excessive Ag appears segregated at the grain boundary. An average composition profile for 14 Ag-rich particles sitting at the boundary was calculated as a function of the distance to the isosurface (referred to as a proximity histogram) and is shown in Fig. 3d. The Ag composition can reach up to over 33 at.%, indicative of a strong tendency for phase separation. An Ag
particle is also directly observed in a low-angle GB in Supplementary Fig. 5, the core of which is indeed free of In/Sb/Te. In addition, In-rich clusters in the range of 5–10 nm in diameter are observed inside the grains but not at the GB or the interface. The composition profile calculated as a function of the distance to the In-isosurface, shown in Fig. 3e, evidences the coexistence of In and Ag, accompanied by a strong depletion in Sb and a slight increase in Te. This suggests that these areas are akin to the quintuple layer with AgSb and InSb, as found in the EDX mapping in Fig. 2.

Crystal orbital Hamilton population and chemical-bonding analysis. Through Cs-TEM and APT, we qualitatively determine the chemical and structural arrangement of crystalline AIST as follows: Sb and Te form Te-Sb-Te-Sb-Te quintuple layers, which are separated by randomly stacked Sb-Sb bilayers; ~3.9 at.% Ag and ~3.3 at.% In substitute the Sb in the quintuple layer, forming AgSb and InSb point defects, whereas excess Ag (above 3.9 at.%) separates in or along GBs. Hence, both Cs-corrected and APT results suggest consistently that there are basic units in AIST with different atomic arrangements, different composition, as well as different dopant distribution. These results also explain the phase segregation in AIST with 8–11 at.% Ag and In, as observed by Iwasaki et al.10, while a single rhombohedral phase was found in AIST with only 3.4 at.% Ag and 3.7 at.% In by Matsunaga et al.13. No In segregation is found because the maximum solubility of InSb in Sb2Te is ~5 at.%26. To understand why AIST favors this particular structural configuration, the formation energies can be obtained from density-functional theory. The corresponding calculations show that this structure, in which both AgSb and InSb defects are located in the quintuple layers, is energetically favorable, as displayed in Fig. 4a. More specifically, the total electronic energy of M1 model with both AgSb and InSb substituents inside the quintuple layer is ~401.18 eV, which is 0.71 eV and 0.92 eV lower than those for the M2 (with one InSb substituent inside bilayer) and the M3 model (with one AgSb substituent inside bilayer), respectively. We also find that Ag and In atoms always prefer to be located in the Sb sites of the quintuple layers in AIST as isolated dopants (see Supplementary Fig. 6).

Further projected crystal orbital Hamilton population (pCOHP) bonding analysis27 in Fig. 4b confirms that the In–Te bonds in model M1 are slightly more stable, by ca. 0.8 eV, than the In–Sb bonds in M2, as reflected by the integrated pCOHP values of ~12.8 and ~13.6 eV. The latter (IpCOHP) values are the bonds’ contributions to the band-structure energy (equivalent to the sum of the Kohn–Sham eigenvalues). In this very Fig. 4, spikes to the right denote bonding, and those to the left indicate antibonding levels28. While this is in line with the total energy of the system, the trend is not reproduced for Ag–Te and Ag–Sb interactions because the latter come out stronger by 0.5 eV, suggesting Ag cannot be stabilized through interactions of covalent character, which COHP analysis mirrors. To address this, additional Mulliken charge analysis was performed also using LOBSTER29,30. The results of this analysis are summarized in Table 1, where we observe a strong difference between the two dopants. While In carries very little charge (and a slightly negative one, so behaving like a mild anion), Ag behaves as a typical...
**Fig. 3** Correlative APT-TEM investigation of grain boundary in crystalline AIST.  
(a) HAADF-STEM image of the needle-shaped AIST specimen along with the diffraction patterns from selected areas evidencing the high-angle grain boundary.  
(b) APT mapping of the AIST showing the segregation of Ag.  
(c) Concentration profiles and ion count of the region of interest highlighted by blue cylinder. Proximity histogram concentration profiles of Ag, In, Sb, and Te for D: 7.5 at.% Ag and E: 5.5 at.% In iso-concentration surfaces. APT results show that ~3.9 at.% Ag and ~3.3 at.% In substitute the Sb in the quintuple layer, and excessive Ag segregates into the grain boundary.

**Fig. 4** Total energy and bonding analysis of AIST with different arrangements.  
(a) Structural images of three typical AIST models (M1–3) including their total electronic energy.  
(b) Projected COHP (pCOHP) plots of In–Te (red) and In–Sb (blue) interactions in models M1 and M2, respectively.  
(c) pCOHP plots of Ag–Te (red) and Ag–Sb (blue) interactions in models M1 and M3, respectively. The integral of the pCOHP up to the Fermi level (IpCOHP) is shown to better quantify the results. The energy axes are referenced to the Fermi level $\varepsilon_F$. 
of an In–In pair near 4.0 Å in its PDF curve. Interestingly, the Ag clusters, observed in AST, completely disappear after adding In. In contrast to the homogenous distribution of indium in IST, In atoms are now located in the two ends of the amorphous AIST. As a result, the intensity of the first peak for Ag–Te pairs in AIST are even higher than in AST, whereas fewer Ag–Sb pairs are observed. The calculated PDF of the amorphous AIST is in good agreement with the experimental data obtained from electron diffraction (Supplementary Fig. 7), implying that the amorphous structure obtained from MD simulation accurately represents the experimentally observed amorphous phase. Thus, adding In prevents Ag atoms from the formation of Ag cluster. In other words, Ag/In atoms are highly localized around Te in amorphous AIST, with Sb filling up the remaining Te coordination sphere, as is observed in the crystalline phase. Note that the distribution of Te atoms is barely altered after incorporating Ag and In, which can be seen from quite similar PDF curves of Sb–Te–Te–Te pairs in ST and AIST. From the mean-square displacements (MSD) in Fig. 5c, we find that the diffusion coefficients \( D_{Ag} \) of Ag (3.61 \( \times 10^{-10} \) m\(^2\) s\(^{-1}\)) and In (2.56 \( \times 10^{-10} \) m\(^2\) s\(^{-1}\)) atoms in AIST are half of that of the systems with isolated Ag (7.31 \( \times 10^{-10} \) m\(^2\) s\(^{-1}\)) or In (3.82 \( \times 10^{-10} \) m\(^2\) s\(^{-1}\)) substituents. This further proves that Ag and In atoms are mutually constrained in the AIST model. It is worthwhile to note that significantly reducing \( D \) would increase the activation energy \( E_a \) of amorphous phase (\( D \propto 1/E_a \))\(^{46}\). Thus, both Ag and In play crucial roles in the stability of amorphous AIST, leading to its higher crystallization temperature compared to ST\(^{35–37}\). For all systems, the Te atoms possess the lowest \( D_{Te} \) and diffuse less compared to the other elements, which plays an important role in stabilizing the network structure. The structural and kinetic features of AIST clearly suggest that the two basic units in the crystalline phase, Ag/In and Sb-enriched areas, can keep their basic frameworks against thermal fluctuations at 600 K.

### Molecular-dynamics simulations of recrystallization

Following the above, determining how the Ag/In or Sb-enriched regions influence the crystallization is of interest. Since AIST is a growth-dominated PCM, here, we focus on the growth process of amorphous AIST. The structural evolution of amorphous AIST on annealing at 600 K were simulated using MD, as shown in Fig. 6a to f. To introduce the nucleus in this process, 45 atoms were fixed at the beginning, including 5 Ag, 5 In, 8 Sb, and 27 Te atoms. Once the crystalline precursors consisting of Ag/In-Te cubes (Fig. 6a) are formed, the precursors first grow along adjacent In atoms in the quintuple layers within the next 20 ps, which is therefore an incubation period for the crystallization. After this period, a clear amorphous-crystalline interface can be observed. The crystalline–amorphous rim grows toward the amorphous area, forming ordered bilayer structures, that is, aligning the Sb-centered octahedra along the c axes of the quintuple layer\(^{12}\).

### Table 1 Mulliken charge analysis of the In and Ag substituents in models M1–M3 as generated by LOBSTER

| In–Te (M3) | In–Sb (M2) | In–Te (M1) | Ag–Sb (M3) | Ag–Te (M2) | Ag–Te (M1) |
|------------|------------|------------|------------|------------|------------|
| Atom       | Charge     | Atom       | Charge     | Atom       | Charge     |
| 2          | In         | 0.09       | 2          | In         | −0.19      | 2          | In         | 0.00       | 1          | Ag         | 0.39       | 1          | Ag         | 0.45       | 1          | Ag         | 0.45       |
| 77         | In         | −0.21      | 15         | Sb         | 0.01       | 76         | Te         | −0.27      | 15         | Sb         | −0.13      | 77         | Te         | −0.31      | 76         | Te         | −0.27      |
| 78         | Te         | −0.10      | 16         | Sb         | 0.01       | 80         | Te         | −0.13      | 16         | Sb         | −0.06      | 78         | Te         | −0.24      | 78         | Te         | −0.24      |
| 84         | Te         | −0.10      | 33         | Sb         | 0.01       | 82         | Te         | −0.27      | 33         | Sb         | −0.13      | 84         | Te         | −0.24      | 82         | Te         | −0.27      |
| 89         | Te         | −0.20      | 34         | Sb         | 0.01       | 86         | Te         | −0.13      | 34         | Sb         | −0.06      | 89         | Te         | −0.30      | 90         | Te         | −0.24      |
| 95         | Te         | −0.20      | 52         | Sb         | 0.02       | 92         | Te         | −0.13      | 52         | Sb         | −0.06      | 95         | Te         | −0.30      | 94         | Te         | −0.27      |
| 96         | Te         | −0.11      | 69         | Sb         | 0.01       | 94         | Te         | −0.27      | 69         | Sb         | −0.13      | 96         | Te         | −0.24      | 96         | Te         | −0.24      |
| Σ          | 0.92       | Σ           | 0.07       | Σ          | −1.20      | Σ           | 0.57       | Σ           | −1.63      | Σ           | −1.53      |

Charges are given for the substituent (first row, bold), the first coordination sphere of the substituent, as well as the sum of the first coordination sphere (last row, bold).
This behavior shows the growth-dominated crystallization mechanism, a substantial difference from the nucleation-dominated mechanism found in GST. As presented in Fig. 6c, the right bilayers (4 layers/60 ps) grow faster than the left ones (3 layers/60 ps) with three Ag atoms. Compared to that, only ~30 ps are required to re-order the In-centered quintuple layer in the center (transition between Fig. 6d, e), while ~90 ps are necessary for the reconfiguration of three bilayers (Fig. 6a through d). This indicates a slight reduction in growth speed through Ag, whereas In accelerates crystallization. After 130 ps, an almost fully crystallized structure can be found, as shown in Fig. 6f. The vast majority of Ag and In atoms are located in the quintuple layer, quite closely resembling the observed crystalline structures in Fig. 2 and Supplementary Fig. 3. Subsequent short-order atom diffusion processes would occur to achieve the energetically favorable crystalline structure.

Discussion

The ~3.9 at.% Ag, through forming unexpectedly ionic Ag–Te bonds, mutually constrain the random diffusion of the atoms in the Ag/In region. Both the ionic Ag–Te bonds and the mutually constrained effect are responsible for the higher crystallization temperature of AIST compared to ST. About 3.3 at.% In atoms accelerate the reconfiguration of quintuple layers, speeding up the crystallization process, which in turn results in the faster...
operation speed of AIST. To sum up, In and Ag in AIST interact to stabilize the amorphous phase, while In atoms speed up crystallization. After forming the Ag/In-enriched quintuple layers, the growth process is subsequently achieved via aligning the Sb-centered octahedra in Sb-enriched regions along the c axes of the quintuple layer, resulting in the growth-dominated crystallization behavior.

According to the aforementioned results, it is reasonable to lower the concentration of Ag in AIST to avoid possible phase segregation. In fact, AIST with 2.3 at.% Ag concentration already possesses sufficient stability against crystallization (at 173 °C). Device cells using the optimized AIST film show the transformation into a low-resistance state (crystallization state) in just 10 ns (Fig. 7a), comparable to DRAM. The speed is twice as fast as the ST-based cell, and six times faster than a GST-based one (see detailed information in Supplementary Fig. 8). The shortened switching process is achieved by acceleration of the crystallization process through In dopant engineering. Moreover, a reduced Ag content indeed prolongs the device lifetime of the cell, over three million cycles, as shown in Fig. 7b, one order of magnitude longer than an AIST-based cell (~10⁷ cycles).

We have now quantitatively determined the distribution of atomic-scale dopants in PCMs by advanced experimental and also theoretical techniques. Transferring the structure obtained by atom-probe tomography and arrived at Ag:In:Sb:Te ~32 pA. The acquisition time was 30 s. The size of EDX mapping were 1024 × 1024 pixels. The probe current was ~32 pA. The acquisition time was 30–80 min.

To get the experimental structure information of the amorphous AIST, we extracted the pair distribution function (PDF) from the electron diffraction data of the amorphous AIST film. The electron diffraction pattern was obtained using JEOL JEM-ARM300F microscopy. The experimental data reduction techniques that used to obtain PDF can be found in refs. 38,39.

**Atom-probe tomography analysis.** Six needle-shaped tips of crystalline AIST were prepared using the standard lift-out procedure by FIB, with a diameter of the apex less than 100 nm. These tips were mounted on a half-cut molybdenum TEM grid, which were then analyzed by JEOL JEM-2100F TEM in bright field mode as well as HAADF mode. The EDX mapping of these tips were also obtained. Subsequently, these tips were put into a 3 × 10⁻¹⁵ mbar high vacuum in local electrode atom-probe (LEAP 5000 XR, Cameca Instruments). Applied a DC voltage of 2–6.5 kV and illuminated by 10 ps laser pulses in the atom-probe tomography, surfaces atoms of the needle-shaped sample were ionized, filed evaporated and subsequently projected onto a position-sensitive detector43. The x- and y-coordinates of the ions registered by the detector, as well as the calculated z-coordinate were used to reconstruct the 3D map. Moreover, these ions can be chemically identified based on time-of-flight mass spectrometry. Reconstruction and analysis of 3D maps were carried out using software IVAS 3.6.14.

**Device preparation and measurement.** One hundred nanometer thick PCM film was deposited on the device with a bottom electrode diameter of 190 nm. Ten nanometer thick TiN and 300-nm-thick Al films are subsequently deposited on the PCM film, severed as the top electrode. The device performances were characterized by a parameter analyzer (Keithley 2400 C) and a pulse generator (Tektronix AWG5200B).

**Bond and charge computational details.** Density-functional theory (DFT) calculations employed the ’D3’ van der Waals correction44 on top of the PBE functional45. Plane-wave basis sets and the projector augmented wave (PAW) method46 were used as implemented in the Vienna Ab Initio Simulation Package (VASP)47–49. The energy cutoff for the plane-wave expansion was set to 500 eV with an electronic convergence criterion of 10⁻⁶ eV. Structural optimization was performed until residual forces fell below 5 × 10⁻³ eV Å⁻¹ and reciprocal space sampling was sampled on Γ-centered k-point grids with densities between 0.02 and 0.04 Å⁻¹. Chemical-bonding analyses of plane-wave data, as well as Mulliken charge analysis, were performed using LOBSTER27–29,46.

**Molecular-dynamics simulations.** Molecular-dynamics simulations were carried out based within the framework of density-functional theory (DFT-MD). The Kohn-Sham equations were solved using the VASP package and the Γ zone center only. The valence electron and core interactions were described using the projector augmented wave (PAW) method, where the valence electrons are 4d⁵5s²5p² for Ag, 4d⁵5s²5p⁴ for In, 5s²5p⁵ for Sb, 5s²5p⁴ for Te. Electron exchange and correlation were treated as described above with a kinetic energy cutoff of 250 eV40,41,47. The convergence criterion was 2 × 10⁻⁵ eV for electronic convergence and 0.2 eV Å⁻¹ for force. Models were first melted at 3000 K for 50 ps with a time step 8t = 2 fs, and then they were relaxed at 600 K for 100 ps. In the simulations, the Parrinello-Rahman (NpT) dynamics with Langevin thermostat was used. The recrystallization...
simulation model (384 atoms, including 16 Ag, 16 In, 256 Sb, and 96 Te atoms) with periodic boundary conditions was acquired as follows: 45 atoms, including 5 Ag, 5 In, 8 Sb, and 27 Te atoms, were fixed during melting and growing processes. The unfixed atoms were maintained at 3000 K for 15 ps to erase the information of crystalline state. The crystal-growth simulation for AIST was performed at 600 K. The total simulation time was 130 ps. The energy cutoff was 250 eV and the time step for the simulations was 3 fs.

Mean-square displacement and Einstein relationship. The mean-square displacement is defined as

$$MSD = \frac{1}{N} \sum_{i=1}^{N} \left( x_i(t) - x_i(t_0) \right)^2$$

(1)

where $N$ is the total number of atoms, $x_i(t_0)$ is the reference position of the $i$th atom at time $t_0$, $x_i(t)$ is the position of the $i$th atom at time $(t + t_0)$. The diffusion coefficient $D$ is determined according to the Einstein relationship

$$MSD = 2D \cdot t$$

(2)

where $t$ is the time of atom movement.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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References

1. Atwood, G. Phase-change materials for electric memories. Science 321, 210–211 (2008).
2. Burr, G. W. et al. Phase change memory technology. J. Vac. Sci. Technol. B 28, 223–261 (2010).
3. Burr, G. W. et al. Overview of candidate device technologies for storage-class memory. IBM J. Res. Dev. 52, 449–463 (2008).
4. https://www.anandtech.com/show/9541/intel-announces-optane-storage-brand-for-3d-xpoint-products.
5. Wuttig, M. & Yamada, N. Phase-change materials for rewriteable data storage. Jpn. J. Appl. Phys. 34, 340–344 (1995).
6. Mulliken, R. S. A new electrostatic scale; together with data on valence states and on valence ionization potentials and electron affinities. J. Chem. Phys. 2, 782–793 (1934).
7. Mulliken, R. S. Electronic structures of polyatomic molecules and valence VI. On the method of molecular orbitals. J. Chem. Phys. 3, 375–378 (1935).
8. Chen, Y.-M. & Kuo, F. C. Effect of Ag or Cu doping on erasable phase-change Sn-Sb-Se thin films. IEEE Trans. Magn. 34, 432–434 (1998).
9. Iwasaki, H., Ide, Y., Harigaya, M., Kageyama, Y. & Fujimura, I. Induced phase changes in group 5B elements. J. Phys. Chem. Solids 326, 223–261 (2010).
10. Chou, C.-C., Hung, F.-Y. & Lui, T.-S. Role of crystallized phases in sheet resistance of amorphous AgSbTe3 chalcogenide film. Scr. Mater. 56, 1107–1110 (2007).
11. Dronskowski, R. & Bölöni, P. E. Crystal orbital Hamilton populations (COHP): energy-resolved visualization of chemical bonding in solids based on density-functional calculations. J. Phys. Chem. 33, 8617–8624 (1999).
12. Maintz, S., Deringer, V. L., Tchougréeff, A. L. & Dronskowski, R. Analytic projection from plane-wave and PAW wavefunctions and application to chemical-bonding analysis in solids. J. Comput. Chem. 34, 2557–2567 (2013).
13. Maintz, S., Deringer, V. L., Tchougréeff, A. L. & Dronskowski, R. Loster: a tool to extract chemical bonding from plane-wave based DFT. J. Comput. Chem. 37, 1030 (2016).
14. Li, W.-L., Ertural, C., Bogdanovski, D., Li, J. & Dronskowski, R. Chemical bonding of crystalline LnB(3) (L=La-Lu) and its relationship with LnB(3) gas-phase complexes. Inorg. Chem. 57, 12999–13008 (2018).
15. Alfred, A. L. Electronegativity values from thermochemical data. J. Inorg. Nucl. Chem. 17, 215–221 (1961).
16. Mulliken, R. S. The 94 elements H-Pu. J. Chem. Phys. 115, 153–163 (1996).
17. Kusuma, T., Suzuki, A., Nishiguchi, T., Shibata, K. & Okuda, M. Phase-change optical recording films with AgInTe2-Sb2Te3 system. Jpn. J. Appl. Phys. 34, 519–520 (1995).
18. Mitchell, D. R. G. & Petersen, T. C. RDFTools: a software tool for quantifying short-range ordering in amorphous materials. Microsc. Res. Tech. 75, 153–163 (2012).
19. Zhou, P. F. Understanding the crystalization behavior of the as-deposited Ti-Sb-Te alloys through real-time radial distribution functions. Nanoscale 7, 9935–9944 (2015).
20. Drigo, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J. Chem. Phys. 132, 154104 (2010).
21. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation to exchange-correlation energy calculations using a plane-wave basis set. Phys. Rev. B 54, 17184–17189 (1996).
22. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169–11186 (1996).
23. Kresse, G. & Furthmüller, J. Efficient ab initio total-energy calculations for metals and semiconductors using a plane-wave basis set. Compu. Mater. Sci. 6, 15–50 (1996).
24. Kresse, G. & Hafner, J. Ab initio molecular dynamics for liquid metals. Phys. Rev. B 47, 558–561 (1993).

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Author contributions
M.Z., X.C. and S.L. prepared the specimens and carried out the TEM experiments. M.Z., B.G. and S.L. carried out the APT experiments and analyzed the APT results. P.M.K. and R.D. performed the COHP calculations. W.S. performed the amorphous structure simulation. T.L. and M.Z. performed the recrystallization simulation. J.S and M.Z. prepared the device and measured the performances. M.Z., P.M.K, B.G., M.W. and R.D. wrote this paper. The project was initiated and conceptualized by M.Z. and Z.S.

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