Atomic structure of AgInSbTe phase change materials: Simulations and a model of crystallization

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Phase change (PC) optical memories are based on the extremely rapid (nanosecond scale) crystallization of nanosized amorphous “marks” in a polycrystalline layer. Until recently, models of crystallization existed for the PC alloy Ge$_2$Sb$_2$Te$_5$ (GST), but not for the important class of Sb-Te based alloys. We have combined density functional simulations on amorphous and crystalline Ag$_{3.5}$In$_{3.8}$Sb$_{75.0}$Te$_{17.7}$ (AIST) with experiment (XRD, EXAFS, hard x-ray photoelectron spectroscopy) to determine their structures and how they differ from GST. Amorphous (a-) AIST has a range of ring sizes, while a-GST has many small rings and cavities, and the local environment of Sb in both forms of AIST is a distorted 3+3 octahedron. We propose a “bond interchange” model (a sequence of small displacements of Sb atoms accompanied by interchanges of short and long bonds) as the origin of the rapid (slow nucleation) crystallization of a-AIST. It differs profoundly from crystallization in a-GST.

1 Introduction

Phase change (PC) materials are chalcogenide (Se, Te) alloys that switch very rapidly between the amorphous (a-) and crystalline (c-) phases. They are used extensively in rewritable high-density data storage, especially in optical recording [Digital Versatile Disc (DVD), Blu-ray Disc]. Information is stored as rows of nanosized amorphous marks in a polycrystalline layer and accessed via the different optical or electrical properties of the two phases. The most common materials are GeTe-Sb$_2$Te$_5$ pseudobinary compounds (Group 1 in Fig. 1a) and Sb-Te binary compounds with small amounts of In, Ag, and/or Ge, e.g. Ag$_{3.5}$In$_{3.8}$Sb$_{75.0}$Te$_{17.7}$ (AIST, Group 2 in Fig. 1a). Recrystallization in the two groups is strikingly different: in Group 1 it proceeds mainly via nucleation inside the marks (Fig. 1b), in Group 2 via crystal growth from the rim (Fig. 1c).

Materials in both groups have superior rewrite speeds, and their amorphous phases are stable at room temperature (RT) for long periods, indispensable characteristics of PC memories. Elements in groups 15 and 16 (including As, Sb, S, Se, and Te) readily form disordered structures that are often short-lived at RT, but compounds containing other elements, such as Ag and In or Ge, can remain amorphous at RT for several decades. High stability implies a low tendency to crystallize, but this process can be accelerated by laser irradiation or electric heating. Crystallization of amorphous Ge$_2$Sb$_2$Te$_5$ (GST) and AIST materials can occur within tens of nanoseconds, so they have both the long-term stability and the rapid switching needed for effective PC memories. An atomic understanding of crystallization is essential, as it is the rate-limiting process in all PC materials.
There have been many studies of crystalline GST (rock salt) and AIST (A7) materials. The average number of $p$-electrons is near 3 in all compositions, suggesting orthogonal bonds with neighbouring atoms and octahedral coordination. Such structures are spatially isotropic or have near cubic symmetry, examples being high-temperature structures of AIST crystals. Much less is known about the structure of the amorphous phases, and the PC mechanism remains the subject of speculation. Recent studies on a-GST include the combination of density functional (DF) / molecular dynamics (MD) and reverse Monte Carlo (RMC) simulations we used to reproduce x-ray diffraction (XRD) and hard x-ray photoelectron spectroscopy (HXPS) data. The structure of a-GST has many small rings with AB alternation ($A$: Ge, Sb; $B$: Te), which act as nuclei in the crystallization process.

However, little is known about the amorphous structures of Group 2 materials, including AIST. The technique used for a-GST [experiment (XRD, HXPS, and EXAFS) combined with DF/MD simulations] has been applied to determine the a- and c-structures of an AIST alloy, $\text{Ag}_{3.5}\text{In}_{3.8}\text{Sb}_{75.6}\text{Te}_{17.7}$. The differences between the structures of GST (Group 1) and AIST (Group 2) have wider implications.

## 2 Density functional calculations and RMC refinement

The combined DF/MD calculations were performed with the CPMD package (Born-Oppenheimer mode), and details of the exchange-correlation functional, the pseudopotential, the plane wave basis, and time steps are given in Ref. 1. The unit cell contained 23 Ag, 25 In, 480 Sb, and 112 Te atoms, and the simulations started at 3000 K in a cubic box (side 27.09 Å), followed by cooling (30 ps) to the melting point (850 K) and data collection.
Cooling to 300 K over 100 ps with gradually decreasing density was then followed by data collection (30 ps) and quenching. The geometry was optimized at the final density (box size 27.57 Å) and refined using the RMC++ code with the XRD structure factor $S(Q)$ and constraints on (a) the average coordination number of all atoms and (b) the distributions of bond angles Sb-Sb-Sb, Sb-Te-Sb, Te-Sb-Sb and Te-Sb-Te. Crystalline AIST (A7 structure) was simulated using 648 atoms in a hexagonal unit cell ($a=25.826$ Å, $c=33.43$ Å). The lattice sites were occupied by 23 Ag, 25 In, 486 Sb, and 114 Te atoms by introducing correlations between Ag/In and Te atoms (Ag/In attracted by Te, Te avoids Te) and optimizing the structure. The cohesive energy is 35 meV/atom lower in a-AIST than in c-AIST (4.07 eV/atom). Further details are given in Ref. 1.

The presence of four elements and the dominance of two (Sb, Te) with similar atomic numbers rule out determining the local structure of AIST by XRD alone, so that we have performed a melt-quenched DF simulation of a-AIST (640 atoms) and refined the structure using a reverse Monte Carlo (RMC) method. The criteria were: (a) agreement with XRD data, (b) a total energy close to the DF minimum, and (c) agreement with the HXPS measurements of electronic structure. The second and third requirements required carefully chosen constraints on bond distances and bond angles, but the resulting $S(Q)$ and $T(r)$ agreed very well with experiment (blue lines in Figs. 2a,b). AIST and GST geometries are shown in Figs. 2c and 2d, respectively. The total energy of RMC-refined a-AIST is only 68 meV/atom above the lowest DF energy. The minority atoms (48 Ag and In atoms in the simulation cell) seldom bind to each other (see Fig. 2c), but often bind to Te (Te avoids itself), suggesting that segregation into Sb and AgInTe$_2$ may occur. The local environment of Sb (75% of all atoms) is very similar to that in the crystal (A7, a distorted octahedron). Cavities are small, and their total volume (7%) is much less than in a-GST (14%). Crystalline AIST has no cavities, c-GST 10%. The difference between the cavities in a-AIST and a-GST is clearly visible in Figs. 2c and 2d, which also show that ABAB squares are common in a-GST, but insignificant in a-AIST.

For the present systems and basis sets, we found satisfactory scaling up to 4096 cores (one rack) of Jugene. The CPMD program package scales better than competing DF/MD programs, but algorithmic changes are clearly needed before it can take full advantage of massively parallel machines.

### 3 Results and discussion

Fig. 2a shows the structure factors $S(Q)$ of AIST and GST obtained using XRD. The c-forms have sharp Bragg peaks (red lines), and the a-forms (black lines) have typical halo patterns. However, oscillations up to the maximum $Q$ value indicate well defined short-range order in a-AIST. Fourier transformation of the $S(Q)$ leads to the total correlation functions $T(r)$ for c-AIST and c-GST (Fig. 2b), which are very similar beyond 4 Å. Small differences exist between the two crystalline forms at shorter distances, e.g. the double peak in c-AIST (2.93 Å and 3.30 Å) and a single peak in c-GST (2.97 Å). The $T(r)$ for the amorphous materials, however, differ significantly: the first peak in a-AIST (2.86 Å) is at a slightly shorter distance than in c-AIST (2.93 Å), but the first peak in a-GST (2.79 Å) is much shorter than in c-GST (2.97 Å). The shoulder on the second peak in a-AIST (3.5 Å, arrowed) is near that observed in the crystalline form (3.30 Å). These differences imply
different crystallization mechanisms; the atomic motion and/or diffusion accompanying the phase change are larger in GST than in AIST, where the bond lengths change little.

The local DF-RMC structure for each element in a-AIST [coordination numbers $N$, bond lengths $r$, and bond orders] is compared with EXAFS measurements (26 K) in Table 1. The coordination numbers from EXAFS measurements for Sb and Te agree well with the calculated values. EXAFS and calculated values for Ag and In show only small differences between the bond lengths.

The DF-RMC structure is consistent with both HEXRD and EXAFS data, and the corresponding density of states (DOS) has been compared with HXPS measurements in
Table 1. Local structure of a-AIST from EXAFS at 26 K and from DF-RMC geometry. $N$: coordination number, $r$: nearest neighbour bond lengths, $N_{\text{bond}}$: chemical coordination number (brackets: c-AIST value).

<table>
<thead>
<tr>
<th>Atom</th>
<th>$N_{\text{EXAFS}}$</th>
<th>$r_{\text{EXAFS}}$</th>
<th>$N_{\text{DF/MD}}$</th>
<th>$r_{\text{DF/MD}}$</th>
<th>$N_{\text{bond}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>3.3 ± 0.5</td>
<td>2.768 ± 0.006</td>
<td>4.4</td>
<td>2.80 ± 0.05</td>
<td>1.9 (2.0)</td>
</tr>
<tr>
<td>In</td>
<td>4.3 ± 0.6</td>
<td>2.826 ± 0.006</td>
<td>3.1</td>
<td>2.85 ± 0.05</td>
<td>2.5 (2.9)</td>
</tr>
<tr>
<td>Sb</td>
<td>3.7 ± 0.3</td>
<td>2.872 ± 0.006</td>
<td>3.3</td>
<td>2.85 ± 0.05</td>
<td>3.1 (3.2)</td>
</tr>
<tr>
<td>Te</td>
<td>2.4 ± 0.4</td>
<td>2.827 ± 0.006</td>
<td>2.5</td>
<td>2.85 ± 0.05</td>
<td>2.5 (2.6)</td>
</tr>
</tbody>
</table>

Ref. 1. As in GST, the amorphous and crystalline phases of AIST have similar HXPS spectra. The calculated DOS of c-AIST differs from the HXPS measurements in that there is a non-zero value at the Fermi energy, i.e. the small band gap semiconductor appears to be “metallic”. DF calculations of this type focus on total energy differences, and the Kohn-Sham eigenvalues shown here commonly underestimate gaps between occupied and unoccupied states. If orthogonal bonds dominate in both phases, the phase change in AIST could occur by rapid bond interchange involving smaller atomic movements than in GST. This is consistent with the smaller change in $T(\tau)$ (XRD) for the two phases of AIST.

The above comparison with XRD, EXAFS, HXPS data shows that our DF-RMC model of a-AIST describes both the atomic arrangement and the electronic structure. A comparison of bonding in a-AIST and c-AIST is essential to understand the differences in PC mechanism, and DF calculations provide information about the bond order (the number of chemical bonds between pairs of atoms) and the effective atomic charge. The chemical coordination numbers $N_{\text{bond}}$ for Sb in AIST, calculated by adding the bond orders to the coordination numbers, provide additional insight. The values for Ag, Sb, and Te of a- and c-AIST are almost the same, as are the bond order profiles of Sb-Sb and Sb-Te. Angular disorder in a-GST breaks the delocalized ("resonant") bonds in c-GST and provides sufficient optical contrast. In AIST, this contrast is due to differences between the covalently bonded amorphous state and the ordered state with delocalized bonds.

The calculated PDF show that: (1) The first peak of the Sb-Sb and Sb-Te distributions are much sharper in a-AIST, and the bond lengths are near those of c-AIST. Both a- and c-AIST have a second maximum at 4.3 Å, which is consistent with a (pseudo)cubic medium range order. (2) Te-Te bonds are rare in a-AIST, while the PDF of c-AIST shows medium-range order with an enhanced peak at 6.2 Å. (3) Ag and In prefer to bind to Te, as seen in the stronger first peak for a-AIST after relaxation. There are few In-Sb bonds.

The RMC-refined DF calculations lead to the local environment around Sb atoms shown in Fig. 3, where both a-AIST (left) and c-AIST (right) show distorted 3+3 octahedra. Each vector shown is the sum of (typically three) short bonds. The norm of a vector is largest for three such bonds, and the vectors are randomly oriented in a-AIST. Laser irradiation or electric heating can lead to successive small atomic shifts that align the vectors along the $c_{11}$-axes of crystalline (A7, hexagonal) cells in the rim, so that the amorphous mark takes on the A7 structure. The essential PC process is a small displacement of the central atom that switches one short (red) and one long (dashed) bond. The close correspondence between the first peaks in $T(\tau)$ in a- and c-AIST is further evidence that the structural change is dominated by bond interchanges among near neighbours.

The atomic interchange alters the orientation of the octahedron, which can adapt to the
crystalline surroundings. The lower panels of Fig. 3 show how the vectors, randomly oriented in a-AIST, align along the $c_{11}$-axis. The octahedra order (A7 structure), the cavities disappear, and the density increases by 7%. The small atomic displacement simply interchanges a strong bond and a weak bond, without requiring bond breaking or diffusion. The PC process is then a sequential, collective motion of Sb atoms, and an avalanche of bond interchanges is consistent with both the instability of amorphous Sb and the rapid phase change in a-AIST and other Group 2 materials.

Figure 3. PC mechanism in a-AIST. Incident laser light causes atomic motion, and the central atom with three short (red) and three long (dashed) bonds moves across the distorted octahedron, interchanging short and long bonds. Green: resultant vector of short bonds. The grey sticks (lower right) correspond to the red bonds (upper right). Atom colours as in Fig. 2c.

The structure and electronic properties of a-AIST and a-GST have been determined using identical techniques, and we note first that the distributions of closed loops (“ring statistics”) differ significantly.1 In a-GST, 40% of the rings are 4-fold or 6-fold, while the peak in the broader distribution in a-AIST is for 5-fold rings, which make up only 15% of the total. Amorphous AIST shows links between rings of various sizes (Fig. 2c), while small rings dominate in a-GST (Fig. 2d). Differences in the topological constraints of ring statistics and cavity concentrations in a- and c-GST imply crystallization processes with changes in bond lengths and coordination numbers (see Fig. 2b). In a-AIST, we propose that a sequence of ring reconstructions via bond interchanges results in 6-fold rings with short Sb bonds, accompanied by small changes in the bond lengths (see Fig. 2b). Crystallization proceeds either from the crystalline area surrounding an amorphous mark (growth-
dominated crystallization) or from a seed that exceeds the critical size for nucleation (slow nucleation for Group 2). The latter occurs in as-deposited AIST films where the amorphous area is larger, and such films crystallize poorly if the surroundings of an amorphous mark are not crystalline. By contrast, many 4- and 6-fold rings in a-GST act as nuclei for crystallization and require larger atomic displacements than in a-AIST. Crystallization starts simultaneously from many such nuclei in the amorphous mark (NaCl fragments, Fig. 2d) and results in small crystal grains. This process is aided by the higher concentrations of cavities (Fig. 2d) and Te atoms, which favour low coordination. The structures suggest a “bond interchange” model as the origin of “growth-dominated” crystallization of a-AIST, whereas the large fraction of crystalline nuclei in a-GST is the origin of the “nucleation-driven” crystallization in GST. Nucleation is slower in AIST, because larger crystalline seeds are needed to impose an A7-type director on the neighbouring amorphous atoms.

4 Conclusions

Density functional simulations (640 atoms in the unit cell) combined with experimental (XRD, EXAFS, HXPS) studies of the AIST alloy Ag$_{3.5}$In$_{3.5}$Sb$_{75.0}$Te$_{17.7}$ have revealed its structure. The local environment of Sb atoms is a distorted 3+3 octahedron in both c- and a-phases, and the bonds in semiconducting a-AIST are slightly shorter (stronger) than in c-AIST (Fig. 2b, Table 1). Crystalline AIST has a distorted octahedral structure and more metallic features, as seen in the electronic DOS. The similar DOS in a- and c-phases is consistent with small atomic displacements during the phase change.

Our model suggests that crystallization of a-AIST is a rapid succession of diffusionless events where the 3+3 octahedra are aligned along the c$_{11}$-axis imposed by the surrounding crystal (see Fig. 1c). Heating or photon excitation causes alignment of the octahedra near the matrix boundary, and crystallites can grow along the laser-scanning direction. The lack of cavities and chemical alternation in a-AIST favour smooth growth. The roles of the dopant atoms (Ag, In) are unclear, but they impede atomic motion near RT and stabilize the amorphous marks. This is consistent with the dopant dependence of the crystallization temperature found in AIST. In a-GST, small rings ("ABAB squares") act as nuclei for crystallization, aided by a higher cavity concentration and the presence of low-coordination Te atoms. Large scale DF simulations of the bond-interchange model should soon be possible.

Acknowledgments

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References


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