

Molecular dynamics study of phase change materials^{*}

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We have simulated, by *ab initio* molecular dynamics (MD), the entire phase-change (PC) cycle in Ge-Sb-Te (GST) materials. Rapid quenching from the melt results in the formation of the amorphous state but, on slower cooling, the models crystallize into the metastable rocksalt crystalline phase. Thermal annealing of the quenched amorphous models also results in crystallization to the same polymorph. Significant numbers of connected, near-planar 4-membered (square) rings exist in the liquid state, and are quenched into the amorphous solid. The presence of these crystal seeds is responsible for the rapid, homogeneously-nucleated crystallization behaviour characteristic of GST PC memory materials.

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1. Introduction

Information storage is essential in this computer age. In the case of non-volatile data-storage technologies, rewritable optical memory has been established for many years in CD and DVD formats based on the rapid, and reversible, laser-induced PC transformation between amorphous (a-) and crystalline (c-) states of Ge-Sb-Te (GST) materials, and relying on the optical-reflectivity contrast between these phases to store bits of information [1]. More recently, a new electronic non-volatile memory technology (phase-change random-access memory, PCRAM) is being developed to replace flash memory, in which voltage-pulse-induced PC transformations are produced between the a- and c- phases of GST materials, information discrimination, in this case, relying on the pronounced electrical-conductivity contrast between the a- and c- phases [2]. Basic unsolved problems, relating to PCRAM, hindering device optimization, include: i) why is crystallization so fast (≤ 1 ns), reversible and homogeneously nucleated (at least for GST)?; ii) how (dis)similar are the atomic structures of the a- and c-states?; iii) what is the origin of the large contrast in the electrical resistivity between the two states, and how can it be controlled?; iv) what is the (defect?) origin of the threshold-voltage switching required to produce a large enough Joule-heating current in the a-phase to crystallize it?; v) what is the origin of multilevel resistance states?; vi) what is the (defect?) origin of the resistance drift with time in the a-state?; vii) is there a lower (device-) size limit to efficient PC operation?; viii) what is the ultimate PC switching speed? Although experimental investigation can shed much light on these issues, such studies can be very challenging in terms of the very small (nm) length scales and (ns) time-scales involved. Therefore, computer

simulation can play an essential role in solving these scientific and technological problems.

2. Simulation method

Molecular dynamics simulation can be used to follow the motion of atoms, by integrating the Newtonian equations of motions if the forces acting on the atoms are known. Constant-volume MD simulations were carried out using the Vienna *Ab-initio* Simulations Package (VASP) [3]. We used the projector augmented-wave method and the PBE exchange-correlation functional [4,5]. The plane-wave cut-offs were set at 175 or 250eV. The outer s and p electrons were treated as valence electrons. Simulations have been made for a variety of GST compositions, along the GeTe-Sb₂Te₃ pseudobinary tie-line (i.e. the compositions Ge₂Sb₂Te₅ (225) and GeSb₂Te₄ (124)), and also GeTe and Ge₁₅Sb₈₅.

For the 225 simulations, for example, cubic simulation boxes (with periodic boundary conditions) contained 63 or 72 atoms, at a density of 6.11 g/cm³, chosen to be slightly smaller than the experimental room-temperature value of the density of the metastable rocksalt structure (6.2 g/cm³ [6]). Two quenching protocols were used to create solid models from the liquid starting state: either a linear cooling ramp or a series of isothermal anneals, each followed by discontinuous decreases in temperature. In addition, isothermal anneals at elevated temperatures were performed on rapidly melt-quenched amodels. In each case, the temperature was controlled by rescaling the velocities of the atoms at every 25th MD step: the integration time step was 2 or 3 fs.

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3. Results and discussion

A key finding of the present study [7] is that whereas rapidly-quenched ($dT/dt = -15$ K/ps) liquid models invariably, and unsurprisingly [8,9], produced solid amorphous structures, much slower cooling (at, say, $dT/dt = -0.45$ K/ps) resulted in crystallization of the models to the metastable rocksalt structure. Liquid 124 and other compositions close to the GeTe-Sb₂Te₃ tie-line, as well as GeTe itself, all of which experimentally show homogeneous crystal-nucleation behaviour [10,11], were also found to crystallize for comparable simulated cooling rates.

Such crystallization events are indicative of the ease of homogeneous crystal-nucleation behaviour in the GST system [10]. We interpret the time (~ 1 ns) needed to crystallize these small (~ 70 -atom) models as representing a lower limit for the time to nucleate homogeneously the metastable rocksalt structure. The homogeneous nucleation time for a-225 has been estimated experimentally [10] to be less than 1ns, in good agreement with the crystallization times found in our simulations.

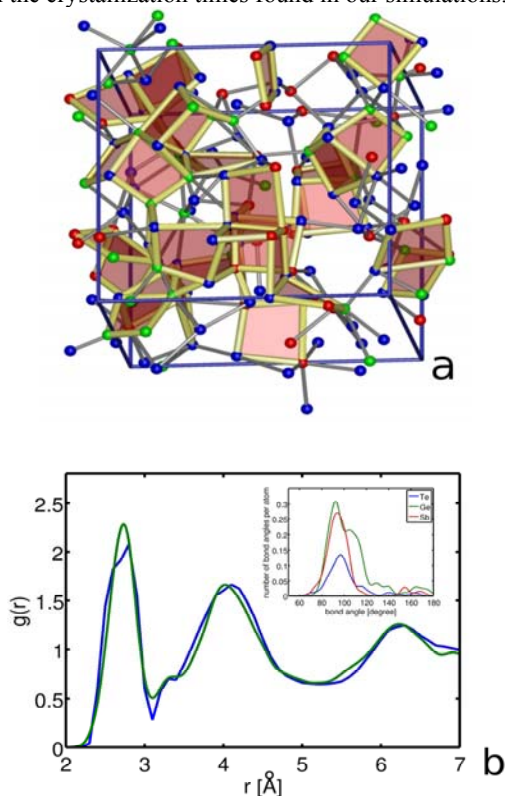


Fig. 1. Structure of a 90-atom model of a-225, relaxed using the CASTEP code [14]: a) atomic configuration showing the presence of (distorted) 4-rings. Colour coding of atoms: Sb, red; Ge, green; Te, blue; b) PDF of the relaxed a-model (green curve) compared with experimental [16] diffraction data (blue curve) for sputtered a-225. The inset shows Ge-Sb- and Te-centred bond-angle distributions.

Crystallization of rapidly-quenched models of a-225 was also observed after isothermal anneals at elevated temperatures (~ 800 K) in comparable times (~ 1 ns). This rapid and facile crystallization is ascribed to the large number of (connected) four-membered square rings, present in the liquid state, that are quenched to form crystal seeds in the a-state (Fig. 1a). Such Ge-Te-Sb-Te square rings are, of course, the characteristic structural motif of the metastable rocksalt crystal structure.

The presence of such crystalline seeds in the a-phase therefore explains why crystallization is homogeneously nucleated and can be so rapid in GST materials: crystalline nuclei do not need to be created *do novo* by thermal fluctuations, but the seeds merely need to grow in the interior of the material.

The structure of the a-state of GST, especially 225, continues to be controversial [12]. EXAFS data [13] indicate that Ge atoms in a-225 are 4-fold coordinated, and the average Ge-Te nearest-neighbour bond length is shorter, and its distribution surprisingly *narrower*, in the a-state than in the metastable rocksalt c-state, where the Ge environment is octahedrally (6-fold) coordinated. Recent other *ab initio* MD simulations [8,9] have also addressed this question of the Ge coordination. Our model of a-225, particularly energy-relaxed using the CASTEP code [14] with Troullier-Martins pseudopotentials [15], has a pair-distribution function (PDF) that agrees very well (including the position of the Ge-Te-containing first peak) with experimental neutron-diffraction data [16] – see Fig. 1(b). The Ge-, Sb- and Te-centred bond-angle distributions, shown in the inset, indicate that most sites have a (distorted) octahedral environment (even though the average first coordination numbers (CNs) are 4(Ge), 3(Sb) and 2(Te)), in that the average bond angle for *all* types of atom is $\sim 90^\circ$. However, the Ge-centred bond-angle distribution also clearly shows evidence for coexistent tetrahedral configurations, with $\theta \sim 109^\circ$, in agreement with other simulations [8,9].

It is instructive to examine (the differences in) atomic-neighbour distances as an indicator of local coordination: any clustering of such distances can then be used as a signature for a particular CN value. We choose a particular type of atom, e.g. Ge, as the origin atom, and then the average interatomic distances between such origin atoms and neighbouring atoms (of *any* type) are sorted according to distance, in ascending order. This analysis is then performed as a function of simulation time during, say, a ramp-like quench of a melt. The results of such an analysis for 225 are shown in Fig. 2, for all 3 types of atom taken in turn as the origin, and for the 10 nearest neighbours, for the case of both slow cooling (leading to a c-product – Fig. 2(a,c,e)) and of rapid cooling (leading to an a-product – Fig. 2(b,d,f)). It can be seen that, at the shortest simulation times corresponding to the highest temperatures (in the liquid phase), the structure is extremely disordered: no clustering of distances is apparent that would allow a well-defined cut-off distance for a first coordination shell in the PDF to be identified. However, the evolution of average n^{th} neighbour distances with decreasing temperature is very interesting: some

distances contract on cooling, while others expand. This process results in a clear clustering of n^{th} -neighbour distances that allows cut-off distances to be identified in

the a/c-solid state (marked by red curves in Fig. 2), and hence average CNs of particular atom types can be evaluated.

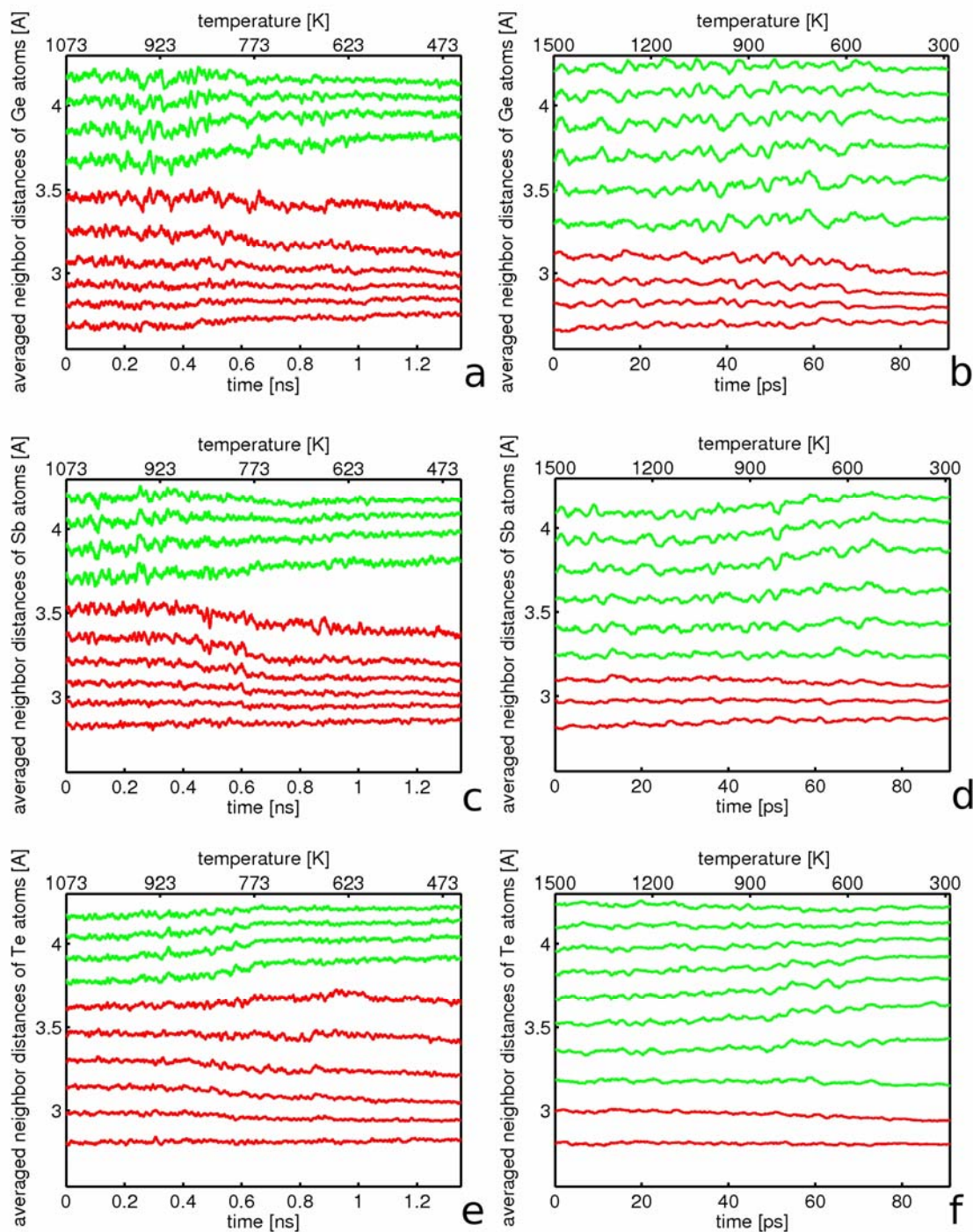


Fig. 2. Evolution of bond lengths in 225 with decreasing temperature (or, equivalently, increasing simulation time) on ramp quenching from the melt, either slowly, leading to the c-state (a, c, e), or rapidly, leading to the a-state (b, d, f). In all cases, one type of atom (Ge, Sb or Te) is chosen as the origin, and the average distances to near neighbours ($n = 1-10$), of all atom types, are sorted according to length. Red curves serve to indicate clustering of these distances in the solid state, and hence define the coordination number for: Ge-centred correlations (a,b); Sb-centred correlations (c,d); Te-centred correlations (e,f).

As a result of this analysis, it is clear from Fig. 2(a,b) that, for the Ge environment in 225, the coordination is 6-fold (octahedral) in the c-state and 4-fold (both distorted octahedral and tetrahedral) in the a-state. Note also from Fig. 2(a,b) that the Ge local environment in the metastable rocksalt c-state is very disordered (e.g. as a result of the presence of vacancies), and as a consequence the distribution of nearest-neighbour (nn) distances is greater, and the average nn distance is smaller in the c-phase than in the a-phase, as found experimentally by EXAFS [13]. For the case of Sb atoms as the origin (Fig. 2(c,d)), the coordination is again 6-fold in the c-state and (marginally) 3-fold coordinated in the a-state (although here the distance clustering is less clear-cut). Finally, for the case of Te (Fig. 2(e,f)), the nn environment in the c-state is 6-fold (but much more disordered as a result of the vacancies on the GeSb sub-lattice for 225) than is the case for Ge- or Sb-centred distances. In the a-state, the Te coordination appears to be 2 (+1).

As a side note, it might be interesting to mention that preliminary MD calculations with photo-generated holes and electrons (similarly to that done in [17]) don't show any significant photo-induced structural change in amorphous GST-225. The reason for this might be that the LUMO and HOMO are not highly localised (as compared for example with pure a-Se, [17]). These preliminary MD simulations suggest that photo induced effects should not play a significant role in the phase change of GST-225.

4. Conclusions

The entire phase-change cycle (liquid-glass-crystal-liquid-crystal) has been simulated, by *ab initio* molecular dynamics, for Ge-Sb-Te memory materials, e.g. Ge₂Sb₂Te₅ and GeSbTe₄. Rapid cooling of the melt produces a glassy phase, but slow cooling of the liquid - or thermal annealing of the glass - results in the production of the metastable rocksalt crystalline phase after ~1ns. The very rapid, homogeneously-nucleated, crystallization of GST materials is ascribed to the presence of connected square 4-rings in the liquid state, quenched into the glassy phase. The average nearest-neighbour coordination numbers of Ge, Sb and Te atoms in the amorphous phase are ~4, 3, 2 respectively, in accord with the 8-N rule. However, the dominant local structural environment of *all* atom types in the glassy state is distorted octahedral (i.e. the average bond angle, θ , for all atoms is ~90°). Nevertheless, there is some evidence for a minority of the Ge sites also having tetrahedral coordination, with θ ~109°. The surprising result from EXAFS measurements, that the nearest-neighbour Ge-Te bond-length distribution is narrower in the amorphous state than in the crystal, is reproduced by

these simulations. The metastable rocksalt structure of Ge₂Sb₂Te₅ is very structurally disordered, as a result of the presence of vacancies in the Ge-Sb sub-lattice.

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