

Crystallisation of phase-change Ga-Sb materials – an *ab initio* molecular-dynamics study

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ABSTRACT

Phase-change materials (PCMs) are being developed as a potential replacement for flash memory devices. Although a large range of compounds have produced promising results experimentally, only $\text{Ge}_2\text{Sb}_2\text{Te}_5$ -based PCMs have been significantly explored using *ab initio* molecular dynamics (AIMD) simulations. In this poster, we present the first AIMD study of the full melt/quench/anneal cycle for Ga-Sb materials - both the stoichiometric composition GaSb and the near-eutectic alloy $\text{Ga}_{16}\text{Sb}_{84}$. Properties related to the local structural environment, as well as the electronic density of states and the optical reflectivity, are compared between the amorphous and crystalline phases for both compositions. It is shown that contrasting electronic and reflective properties of each crystalline model can be attributed to different mechanisms of crystallization from the amorphous state: Sb transforms from an octahedral-like to a tetrahedral geometry in GaSb, whereas Ga transforms from a tetrahedral to an octahedral-like configuration in $\text{Ga}_{16}\text{Sb}_{84}$.

Key words: phase change, GaSb, $\text{Ga}_{16}\text{Sb}_{84}$, PCRAM, *ab initio*, molecular dynamics

Introduction

Phase-change materials (PCMs) based around the composition $\text{Ge}_2\text{Sb}_2\text{Te}_5$ have received a large amount of attention for non-volatile electronic-memory applications since their initial use in rewriteable optical discs^[1]. The crystallisation mechanism has been explored both experimentally^[2] and through *ab initio* simulations^[3], including the effect of dopants^[4] and the role of vacancies^[5]. However, the desire to keep Te out of Si CMOS manufacturing lines^[6], as well as improving data-retention properties, has led to a search for other suitable material compositions.

Sb-based PCMs have been explored due to the rapid room-temperature crystallisation of pure Sb. A large number of Sb-X binary systems have shown phase-change characteristics^[7]; however they often suffer from phase separation, leading to premature failure^[8]. For the Ga-Sb system, there is some evidence this can be suppressed through cell design^[9], or by using a stable stoichiometric mixture^[10]. The low melting point of Ga (27.9°C) is ideal for lowering the power requirements of real memory devices.

We have completed the first *ab initio* molecular dynamics simulations of the melt-quench-anneal phase-change cycle for Ga-Sb, for compositions of both stoichiometric GaSb and the near-eutectic $\text{Ga}_{16}\text{Sb}_{84}$. For the amorphous and crystalline models, we determine the local atomic structure, electronic density of states and optical-reflectivity curves. The changes in local structure associated with crystallisation have been identified and we show how they affect the contrasting properties between the different crystal structures.

Simulation

All molecular-dynamics (MD) calculations were performed with the Vienna *ab initio* Simulation Package (VASP)^[11], using the projector augmented-wave method^[12] and the Perdew-Burke-Ernzerhof exchange-correlation functional^[13]. The plane-wave cutoff was set at 172eV, an integration time step of 5fs was used and the outer s and p electrons were treated as valence electrons. MD steps were calculated at the gamma point and the temperature was controlled by velocity scaling.

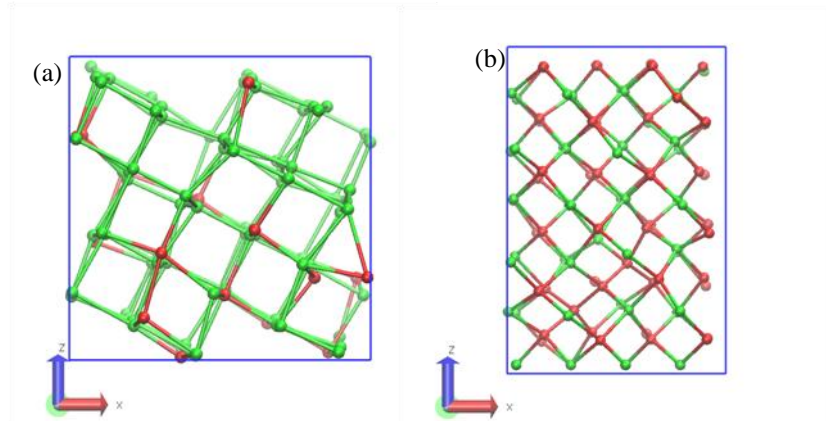
We model the melt/quench process by performing an initial mixing of 20ps at 3000K, followed by liquid equilibration at 1200K for 40ps and a quench to 300K at -15K/ps. To induce crystallisation the resulting amorphous structure was annealed at $T_{\text{anneal}} = 550\text{K}$, for a time period τ . For $\text{Ga}_{16}\text{Sb}_{84}$, a cubic simulation cell was used at a density of 6.47g/cm^3 , the model size was 100 atoms and was annealed for $\tau = 180\text{ps}$. For $\text{Ga}_{50}\text{Sb}_{50}$, a rectangular simulation cell was used at a density of 5.60g/cm^3 , the model size was 96 atoms and the simulation box was templated with a (001) layer of Sb, and was annealed for $\tau = 880\text{ps}$. Density-of-states and reflectance calculations were performed on relaxed structures with a $2 \times 2 \times 2$ k -point mesh. Relaxed structures were further annealed at room temperature (300K) to determine bond statistics.

Results

Both compositions were observed to crystallise fully within their annealing time periods, the progress of crystallisation being tracked using a Fourier-transform method^[3]. Visual inspection of the structures indicates two different crystal lattices for the different compositions [fig1].

Figure 1

Snapshots of crystalline structures for: (a) - $\text{Ga}_{16}\text{Sb}_{84}$, 100-atom model, annealed at 550K for 180ps; (b) - $\text{Ga}_{50}\text{Sb}_{50}$, 96-atom model, annealed at 550K for 880ps. Ga – red, Sb – green.



Analysis of the bond-angle distributions indicates two differing crystallisation mechanisms for the compositions [fig2]. The amorphous phases for both $\text{Ga}_{16}\text{Sb}_{84}$ and $\text{Ga}_{50}\text{Sb}_{50}$ show very similar coordination environments, Ga atoms being split between tetrahedral and octahedral-like coordinations and Sb adopting an octahedral-like coordination. Upon crystallisation, we see Ga transforming to an octahedral-like coordination in $\text{Ga}_{16}\text{Sb}_{84}$ to generate a cubic-like crystal structure. In $\text{Ga}_{50}\text{Sb}_{50}$, Sb transforms to a tetrahedral coordination; overall a zinc blende-like structure is formed, with substitutional defects on approximately 6% of the lattice sites.

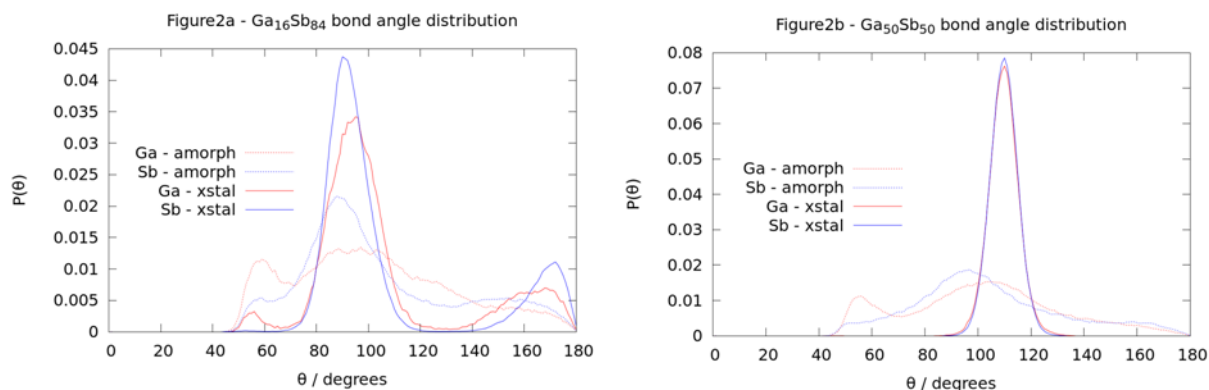


Figure 2 – Bond-angle distributions for $\text{Ga}_{16}\text{Sb}_{84}$ (a) and $\text{Ga}_{50}\text{Sb}_{50}$ (b) compositions, averaged over 10ps of a room-temperature equilibration. In (a), we see that the primary transition is of Ga from a tetrahedral to a more octahedral-like coordination. In (b), the transition is much more pronounced, with the primary change for Sb being from octahedral to tetrahedral coordination

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References

1. G.-F. Zhou, *Mater. Sci. Eng. A* 2001; 304–306.
2. B.-S. Lee *et al*, *Science* 326 (2009). 980-984
3. J Hegedus, *Nat. Mater.* 7 (2008), 399-405
4. R. Kojima *Jpn J. Appl. Phys.* 37 (1998), 2098
5. T.H. Lee, *Phys. Rev. B* 84 (2011), 094124
6. C Cabral, *Appl. Phys. Lett* 90 (2007), 051908
7. L. van Pieterse, *J. Appl. Phys.* 97 (2005), 083520
8. C Cabral, *Appl. Phys. Lett.* 93 (2008), 071906]
9. C.-C. Chang, *CrystEngComm.* 13 (2011), 5642-5645
10. S. Raoux, *Phys. Status Solidi B* 249 (2012), 1999-2004
11. G. Kresse, *Phys. Rev. B* 47 (1993), 558
12. P. Blochl, *Phys. Rev. B* 50 (1994), 17953
13. J. Perdew, *Phys. Rev. Lett.* 77 (1996), 3865

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