Computer-aided deposition of Ga_xSb_{1-x} thin films

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ABSTRACT

Phase change materials function because the amorphous and crystalline phases have distinct electronic and optical properties, and the transition between them can occur on the timescale of nanoseconds. The determination of the structures involved has challenged both theory and experiment. Atomistic simulations on phase-change materials have focused on melt-quenched samples, and both system size and quench time have posed challenges. Here, we have performed density functional/molecular dynamics simulations of thin films of Ga_xSb_{1-x} alloys (x=0.125, 0.25, 0.333, and 0.50), which belong to the family of Sb-rich PCMs. We grow deposited samples of 528 atoms at 300 K on a fixed template by generating sparse layers (gas) of the material in question. The low atomic mobility and randomized deposition procedure result in structures with a significant number of Ga-Ga bonds.

Key words: phase change materials, deposition, Ga/Sb alloys, density functional, molecular dynamics

1. INTRODUCTION

Atomic structure is crucial for the function of phase change materials (PCM). There has been much focus on the amorphous and crystalline phases of PCMs, which have distinct electronic and optical properties and ultra-fast phase transition. The determination of disorder structures challenges both theory and experiment, and atomistic simulations commonly consider melt-quenched (MQ) samples, where the system size and time scale are limited. Recently, we presented results of massively-parallel density functional (DF) simulations of the as-deposited (AD) amorphous structure of the prototype phase change material $Ge_2Sb_2Te_5$ [1] by studying a 648-atom sample generated by computer-aided deposition at 300 K. The results were compared with those for a 460-atom MQ sample [2]. The AD structure differed from MQ in essential ways [more tetrahedral Ge atoms and wrong bonds, less *ABAB* squares (*A*=Ge,Sb; *B*=Te)], which resolved the contradiction between measured and calculated Ge-Te bond lengths and explained the large differences in crystallization speeds.

We report here a computer-aided deposition study on Ga_xSb_{1-x} alloys (x=0.125, 0.25, 0.333, and 0.50), which belong to the family of Sb-rich PCMs where the re-crystallization occurs via a growth-dominated mechanism [3,4]. We focus on the surface structure and properties, with the aim of generating 3D bulk configurations for comparing with MQ structures with the same composition. In addition to methods based on melt-quench and deposition, we have generated amorphous configurations for other chalcogenide alloys using a combination of an experimentally constrained reverse Monte Carlo (RMC) method and DF simulations [4-6].

2. METHODS

We use the CPMD code [7] for DF/MD simulations in the Car-Parrinello mode. The exchange-correlation energy functional uses the PBEsol [8] approximation, and the time step is 0.1693 fs (7 a.u.). Simulations have been carried out in an NVT ensemble with cubic simulation cell, periodic boundary conditions and a single point (**k**=0) in the

Brillouin zone. The temperature is controlled by Nosé-Hoover thermostat (chain length 4, frequency 800 cm^{-1}), and we use Troullier-Martins pseudopotentials [9] with a cutoff of 20 Ry for the kinetic energy of the plane-wave basis.

We deposit samples of 528 atoms for each composition by sequentially generating 20 random sparse layers of atoms on a fixed template at 300 K and performing DF/ MD for hundreds of picoseconds. The film models for GaSb, $GaSb_2$, $GaSb_3$ and $GaSb_7$ were generated by first randomizing a 2.35 Å layer of 48 fixed atoms with a 2.60 Å minimum distance between the atoms for each composition. Twenty sparse layers of 24 atoms each ("gas", layer thickness 4.0 Å, min. interatomic distance 3.2 Å) were then added to the structures, which were relaxed for 4 ps at 300 K before the next layer was added. After relaxing the last sparse layer the structures were equilibrated for 10-20 ps.

3. RESULTS & DISCUSSION
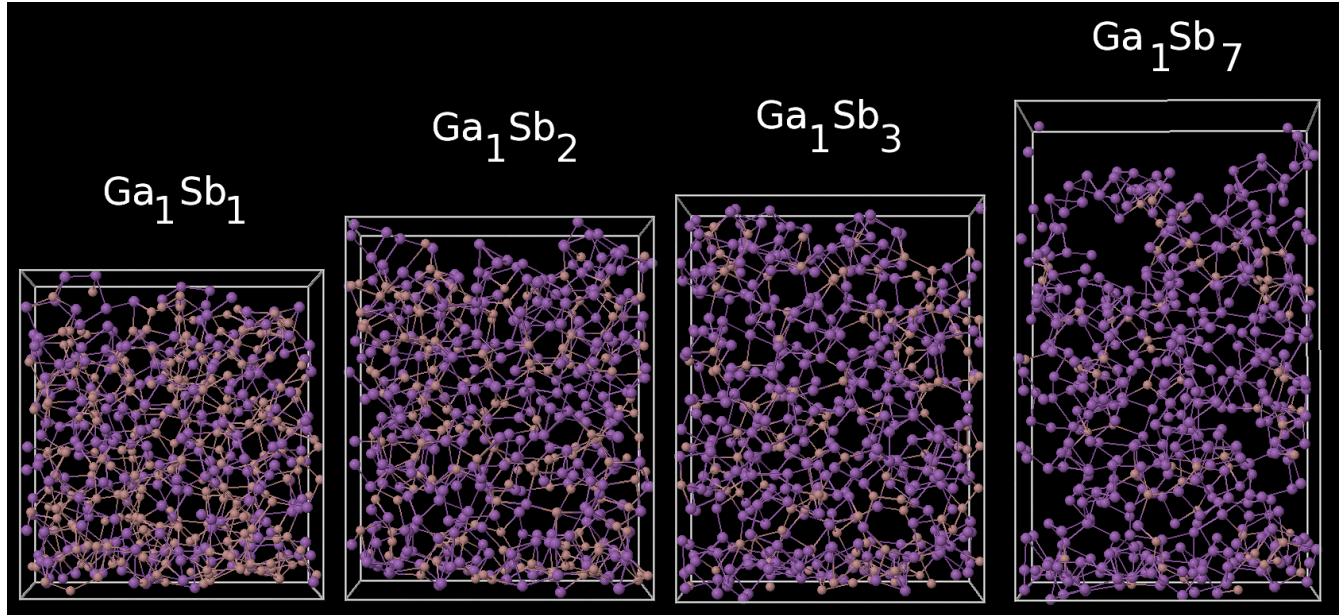
Figure 1: Structures after DF/MD equilibration. Gallium atoms are shown in tan, antimony atoms in purple.

Figure 1 shows the film structures of the Ga_xSb_{1-x} compositions. The films are periodic in the lateral dimensions, and there is a vacuum of 10 Å in the vertical direction in each case. As the Sb composition increases, the structure becomes more porous and the film thickness grows. The extended vertical dimension (low density) of the $GaSb_7$ structure suggests that the final geometry will differ from an experimentally deposited surface, where the relaxation takes much longer and the kinetic energy of incoming atoms is higher. This feature is ascribed to Sb atoms which prefer a 3+3 coordination (short/long bonds) [3], and DF/MD does not appear to allow a full relaxation of such network, especially for long bonds. For the other compositions, the higher Ga content increases chemical coordination and produces film structures with higher density. In $GaSb_3$ and $GaSb_7$, we observe cluster formation of a few Sb atoms (mostly chemically inert Sb_4), which separate readily from the surface and are more mobile. This suggests that etching might also occur in the experiments, which can change the Ga/Sb composition near the sample surface.

Figures 2(a) and (b) show the density of atoms as a function of z-coordinate. The $GaSb_2$ film is approximately 2 Å thicker than the GaSb film, due to the increased Sb-content, and is slightly less uniform in density. The increased weight of Sb at the surface reflects its preference for lower coordination and cluster formation in Sb-rich alloys. The pair distribution functions (PDFs) in Figures 2(c-e) show significant contributions of all bond types. The PDFs have been computed for equilibrated samples from DF/MD simulations of 10 and 20 ps for GaSb and $GaSb_2$, respectively. The bond distances are: 2.50/2.50 Å for Ga-Ga, 2.70/2.72 for Ga-Sb, and 2.90/2.88 for Sb-Sb. The first PDF peaks of the two compositions are not different but there are differences in the height and distance of second and subsequent peaks. The reduced weight of the 2nd peak of Sb-Sb distribution, in particular, is related to the changes in density.
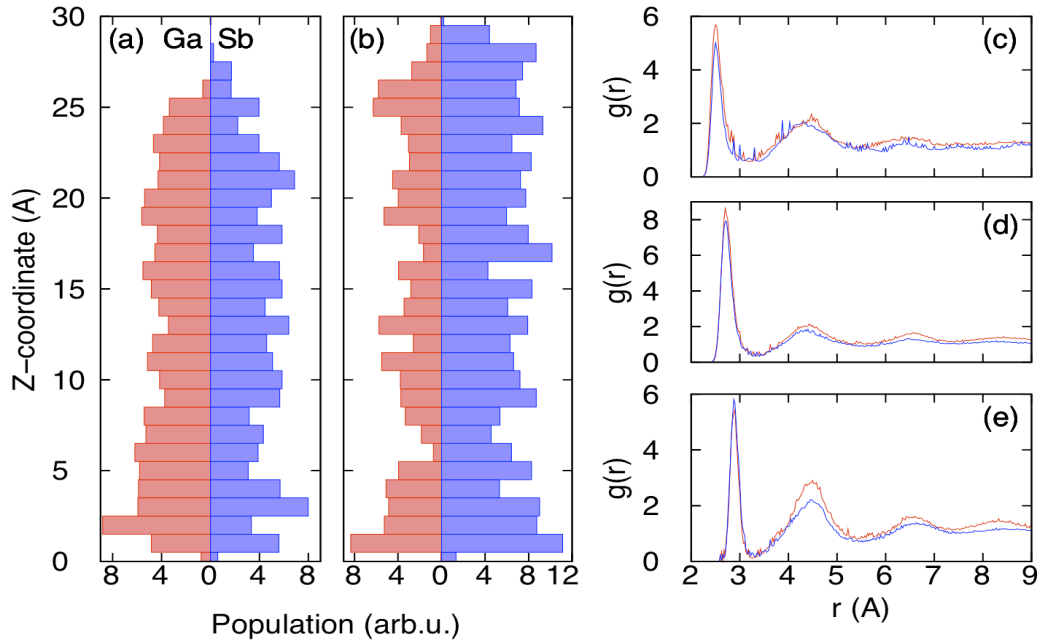
Figure 2: Laterally averaged distributions of atoms in (a) GaSb and (b) GaSb$_2$ structures. Red: Ga, blue: Sb populations. Zero of the *z*-coordinate corresponds to the bottom of the film, where the fixed atoms are located (two lowermost bars). (c) Ga-Ga, (d) Ga-Sb, (e) Sb-Sb PDF. Red: GaSb, blue: GaSb$_2$.

4. CONCLUDING REMARKS

We have simulated computer-aided deposition of Ga$_x$Sb$_{1-x}$ films (x=0.125, 0.25, 0.333, and 0.50), which promise future applications in phase-change memory [3]. This is a progress report on a project to determine the structures of as-deposited and melt-quenched structures of the bulk materials for each composition. We have found that the reduced atomic mobility in the low-T deposition process results in the excess formation of Ga-Ga and Sb-Sb bonds (the latter applies for compositions with x=0.333 and 0.50). Furthermore, the limitations in the simulation become evident for Sb-rich films, where significant porosity may be an artifact of the simulation. This phenomenon will not affect the final 3D bulk models, because it will subsequently be removed by a gradual compression.

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Biographies

J. Kalikka studied Physics at the University of Jyväskylä, Finland, obtaining his Master's degree in 2008. He will complete the work for his Ph.D. (under Jaakko Akola) in 2012. The main focus has been on phase change materials, particularly simulations of crystallization.

J. Akola studied Physics at the Universities of Helsinki and Jyväskylä, Finland, obtaining his Ph.D. at Jyväskylä under Matti Manninen. After five years as a Post-doctoral Researcher at the Forschungszentrum Jülich, Germany, he returned in 2005 to the Nanoscience Center in Jyväskylä. He is currently Academy Research Fellow in the Tampere University of Technology, Finland, where he heads the Molecule and Materials Modeling (MMM) group. His fields of interest include classical, tight-binding, and density functional simulations of materials, nanoparticles, and biological systems.

R. O. Jones obtained his B.Sc. Hons (Physics) at the University of Western Australia in Perth and his Ph.D. at the University of Cambridge, England under Volker Heine. He spent three years as a Post-doctoral Associate at Cornell University before joining the Forschungszentrum Jülich. His main focus for over 30 years has been on density functional theory and its applications to many ordered and disordered systems (solids, surfaces, atomic clusters, molecules, polymers, biological molecules, …)