Density functional simulations of structure and polymorphism in Ga/Sb films

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Abstract

Thin films of gallium/antimony alloys are promising candidates for phase change memories requiring rapid crystallization at high crystallization temperatures. Prominent examples are the stoichiometric form GaSb and alloys near the eutectic composition GaSb$_{7}$, but little is known about their amorphous structures or the differences between the ‘as-deposited’ (AD) and ‘melt-quenched’ (MQ) forms. We have generated these structures using 528-atom density functional/molecular dynamics simulations, and we have studied in detail and compared structural parameters (pair distribution functions, structure factors, coordination numbers, bond and ring size distributions) and electronic properties (densities of states, bond orders) for all structures. There is good agreement with x-ray diffraction data from deposited films of GaSb, and there is evidence for Sb segregation in GaSb$_{7}$.

(Some figures may appear in colour only in the online journal)

1. Introduction

Phase change (PC) materials are chalcogenide alloys for which nanosized bits in a thin polycrystalline layer can be switched reversibly in nanoseconds between ordered and disordered phases. Phase changes are achieved by laser irradiation or resistive heating and can be monitored by changes in resistivity or optical properties. These processes are the basis for rewritable optical storage (digital versatile disc DVD, Blu-ray Disc) and are promising candidates for future computer random access memory (PC-RAM) [1]. The amorphous bits should be stable at room temperature for several decades while crystallizing very rapidly at higher temperatures, and the additional requirement for significant optical contrast between the phases rules out many materials. The PC materials that have been studied most include GST alloys (GeTe$_{2}$,(Sb$_{2}$Te$_{3}$)$_{1-x}$, particularly Ge$_{2}$Sb$_{2}$Te$_{5}$ (GST-225), and Sb-rich compounds such as Ag/In/Sh/Te (AIST) alloys. Compounds of the latter family recrystallize rapidly and are very stable [2–4], but the low contrast between phases and their limited cyclability due to segregation can restrict their use in memory devices [4].

Experimental advances and large-scale molecular dynamics simulations have improved our understanding of the phase changes in GST [5–13] and AIST [14] families significantly. However, these materials do not show dynamic RAM (DRAM) performance, and their crystallization temperatures $T_x$ are too low for applications in the automobile industry. The search for materials with short crystallization times $\tau_x$, high $T_x$, and a large resistance contrast, if possible without the toxicity of Te, has included alloys of Ga and Sb [15–17]. GaSb, a direct band gap semiconductor used as an infrared detector, has a cubic (zinc blende) crystal structure and a
high $T_x$, and as-deposited amorphous GaSb films crystallize rapidly [17, 18].

In spite of the promise of GaSb, compositions near the eutectic (Ga$_2$Sb$_8$) have received more attention. The crystallization temperature for Ga$_4$Sb$_6$ (220°C), for example, is much higher than that for GST-225, and the high activation energy of crystallization ($\sim$4.6 eV) leads to ultra-long data retention (10 years at 162°C) [15], which can be tuned by varying the composition [2, 15]. Time-resolved x-ray diffraction (XRD) measurements show that GaSb crystallizes at 315°C, and Ga$_{13}$Sb$_{87}$ (GaSb$_7$) crystallizes at 200°C [17]. While the ordered form for GaSb could be identified unambiguously, it is unclear whether Ga$_{13}$Sb$_{87}$ crystallizes in the rhombohedral (A7) structure for Sb or a mixture of the Sb and GaSb crystal phases. The segregation of Sb-rich Ga/Sb alloys into GaSb and Sb is an important issue for their stability [16, 18, 19]. Although this effect is weaker in very thin (~3 nm) films of Ga$_{16}$Sb$_{84}$ [16], repeated cycles in PC-RAM devices may lead to phase separation.

Very little is known about the structure of amorphous Ga/Sb films and the nature of their structural phase transition, and we extend here our density functional (DF)/molecular dynamics (MD) simulations on GST and AIST alloys [12–14] to these alloys. Many simulations involve rapid cooling from the liquid phase (‘melt-quenched’, MQ), while measurements are often performed on vapour deposited (‘as-deposited’, AD) samples. MQ and AD samples can have similar [20] or quite different compositions and properties, including different crystallization speeds [4, 17, 21], and both are simulated here. The differences in Ge$_2$Sb$_2$Te$_5$ could explain the discrepancies between experimental measurements and computer simulations [22]. Chalcogenide glasses containing Ga are also used in infrared optics and waveguides [23], and they were the first to show rewritable memory features in thermally drawn fibres [24]. Ga has also been studied as a dopant in Sb–Te alloys: it results in more rapid crystallization [24]. Ga has also been studied as a dopant in Sb–Te alloys: it results in more rapid crystallization [24]. Ga and Sb$_7$ have been performed with 528 atoms in the unit cell. We aim to provide the first detailed structural information about these systems and to indicate their similarities and differences, but not to speculate on possible phase change mechanisms. In section 2 we outline the methods of computation and analysis, in section 3 we describe and discuss the structures and electronic properties, and we summarize our work in section 4.

2. DF/MD computations

Car–Parrinello calculations [26] were carried out with the CPMD program [27] using a time step of 0.1693 fs (7 a.u.), an effective electron mass of 1200 $m_e$, and the PBEsol approximation [28] for the exchange–correlation energy. We studied NVT ensembles (constant number of particles $N$, volume $V$, and temperature $T$), using a simulation cell with a square base (25.86 Å side) and variable height, periodic boundary conditions, and a single point (k = 0) in the Brillouin zone. The temperature was controlled by a Nosé–Hoover thermostat (chain length 4, frequency 800 cm$^{-1}$). Scalar-relativistic pseudopotentials [29] were used, with a kinetic energy cutoff of 20 Ryd for the plane-wave basis.

The deposited slabs of 528 atoms were prepared using the procedure described in [22]. First, a randomized layer (template) of 2.35 Å thickness and 48 atoms (minimum separation 2.60 Å) was generated for each alloy and the coordinates fixed until compression began. Twenty random sparse layers with 24 atoms (‘gas’, minimum interatomic distance 3.2 Å) were then placed sequentially on this template, with a ‘vacuum’ of 10 Å separating each system from the replica above. The system was relaxed (4 ps at 300 K) after each layer was added, and finally equilibrated for 10–20 ps. The laterally averaged atom density decreased gradually to zero with increasing height (z) instead of having a distinct edge, in particular for GaSb$_7$. The difference between the lowest and highest atom in the z-direction was 27.88 Å and 42.39 Å for GaSb and GaSb$_7$, respectively.

AD structures (figures 1(a) and (c)) were then prepared by decreasing slowly the size of the simulation cell in the vertical (z) direction (the minimum distance between the atoms at the top and bottom of the film was set initially to 3.5 Å), without changing the lateral dimensions. DF/MD runs (61–65 ps, nonlinear compression of 0.067–0.5 Å ps$^{-1}$) were then performed to compress the structures to the required bulk density. The compression was most rapid initially, slowing later to increase relaxation, and the total time for each AD simulation was over 150 ps. The target bulk densities were estimated from the known densities of crystalline GaSb and Sb, reduced by 5% to account for amorphization, and refined by calculating the stress tensor. The final values were 0.0336 atoms Å$^{-3}$ (5.35 g cm$^{-3}$) for GaSb and 0.0290 atoms Å$^{-3}$ (5.55 g cm$^{-3}$) for GaSb$_7$. The final simulation cells were 25.86 $\times$ 25.86 $\times$ 23.48 Å$^3$ (GaSb) and 25.86 $\times$ 25.86 $\times$ 27.22 Å$^3$ (GaSb$_7$).

The MQ structures (figures 1(b) and (d)) were obtained from the AD samples by heating above the melting temperature and quenching. The initial temperature was 1000 K for GaSb and 900 K for GaSb$_7$. The mean square displacement of the atoms was monitored during the melting phase to ensure that the structure was liquid. Equilibration times at the initial temperatures (1000 and 900 K) were 12 ps for GaSb and 10 ps for GaSb$_7$. The structures were then quenched to 300 K in 48 and 50 ps for GaSb and GaSb$_7$, respectively, so that the MQ time for both structures was 60 ps. After the quench, the structures were equilibrated at 300 K for 5 ps, followed by data collection from 5 ps simulations for both the AD and MQ samples. The average pressures for the MQ phases were 1.3 kbar for GaSb and 4.1 kbar for GaSb$_7$. The electronic densities of states (DOS) and chemical bond orders were computed for the final structure. Coordination numbers and atomic environments calculated using bond distances (variable cutoff) and bond orders (chemical coordination, cutoff of 0.3 for counting bonds) gave consistent results. Partial coordination numbers,
structure factors, and ring statistics were calculated using the ISAACS program [30]. We define cavities (nanosized voids) as in [5] and use the same cutoff (2.8 Å) for the test sphere.

3. Results and discussion

3.1. Pair distribution functions, coordination numbers, structure factors

The partial pair distribution functions (PDF) are shown in figure 2, and the corresponding maxima and minima are given in table 1. X-ray diffraction (XRD) measurements have been carried out by Shevchik and Paul [31] on GaSb films deposited on Cu substrates, and the positions of the first two peaks in the PDF (2.67 ± 0.03 Å, 4.30 ± 0.05 Å) agree well with our values (2.68, 4.32 Å (AD), 2.70, 4.36 Å (MQ), total PDF with XRD-weights). The first peak in the calculated Ga–Ga PDF (2.48 Å) is remarkably close to the nearest neighbour separation in crystalline (orthorhombic) Ga (2.484 ± 0.012 Å) [32], where six additional near neighbours lie between 2.69 and 2.79 Å. The pairs of atoms forming the short bonds are often referred to as ‘Ga dimers’, but we note that the experimental ground state of free Ga$_2$ ($^3\Sigma_g^-$) [33] has a significantly longer bond [34, 35]. The short bond found here and in other extended systems is related to the higher-lying $^3\Sigma_g^-$ state of Ga$_2$.

Ga–Sb bonds are the most abundant in both the AD and MQ structures of GaSb, but the number of homopolar bonds decreases significantly during MQ. The corresponding coordination numbers are shown in table 1. The chemical coordination numbers, where we consider bonds with a bond order $\geq 3$, are lower than the coordination numbers calculated with radial cutoff distances (atomic structure). There is a small increase (0.4) in the Ga–Sb chemical coordination between AD and MQ, but the change (reduction by 0.4–0.6) is significant for Ga–Ga. The Sb–Sb coordination is 0.3 lower in MQ than in AD.

The coordination numbers are plotted in figure 3 as a function of cutoff radius. The figure also shows the shift between AD and MQ structures, with MQ having fewer homopolar bonds. The total coordination is approximately
Figure 2. PDF for GaSb (a)–(c) and GaSb$_7$ (d)–(f) for atom pairs Ga–Ga (a), (d), Ga–Sb (b), (e) and Sb–Sb (c), (f). Red: AD, blue: MQ.

four for all structures, and a tetrahedral environment is also consistent with bond angle distributions. This is evident for GaSb in figures 4(a) and (b). The nearest neighbour analysis of atomic configurations is given in table 2, which shows that 10.6/11.4% of Ga and 25.4/20.1% of Sb atoms are threefold coordinated. Threefold-coordinated Ga atoms are more common in MQ, but the opposite is true for Sb. The most general neighbour configurations are Ga$_2$Sb$_2$, GaSb$_3$ and Sb$_4$ for Ga, and Ga$_2$Sb$_2$, Ga$_3$Sb and Ga$_4$ for Sb. Ga has more Sb neighbours (3–4) in MQ than in AD, while Sb has fewer Sb neighbours (0–1). The XRD measurements of Shevchik and Paul [31] indicate that bonds between like atoms (‘wrong bonds’) must be present. There are no homopolar bonds in crystalline GaSb.

The PDF (figure 2) and coordination numbers for GaSb$_7$ (table 1) change little from AD to MQ, apart from a slight shift in Ga coordination from Ga–Ga to Ga–Sb. This is also reflected in the coordination numbers as a function of cutoff radius (figure 3), where the graphs are indistinguishable except for Ga–Ga, where the MQ curve is lower. The overall coordination numbers suggest tetrahedral coordination for Ga and defective octahedral (threefold) coordination for Sb (see the GaSb$_7$ structures in figures 4(c) and (d)). Bond distances and the Ga–Sb PDF are very similar to those in GaSb. The Sb–Sb PDF show differences in the second maximum, which
Figure 3. Partial coordination numbers for GaSb and GaSb$_7$ as a function of cutoff distance for (a) Ga–Ga, (b) Ga–Sb, (c) Sb–Ga and (d) Sb–Sb. GaSb: red: AD, blue: MQ; GaSb$_7$: magenta: AD, black: MQ. Dashed lines at 3.2 Å mark typical cutoff distances.

Figure 4. Details for the GaSb ((a) AD, (b) MQ) and GaSb$_7$ ((c) AD, (d) MQ) structures. The inset shows a threefold ring formed by three distorted octahedral Sb atoms. Orange: Ga, purple: Sb.

is more pronounced for GaSb due to tetrahedral coordination for Sb. The ν-shaped first minimum in GaSb$_7$ has a steeper left slope, similar to that found in Sb-rich AISI, where it was ascribed to defective octahedral 3 + 3 coordination [14].

The local environments for the AD and MQ structures of GaSb$_7$ (table 2) differ slightly, although the Ga environment in MQ shows more Sb-rich environments (from GaSb$_3$ to Sb$_4$ and from GaSb$_2$ to Sb$_3$). This is evident in the Ga partial
Table 1. First maxima ($r_{\text{max}}$) and minima ($r_{\text{min}}$) in the partial PDF (Å), coordination numbers $N$ for the corresponding $r_{\text{min}}$, and chemical coordination numbers $N_{\text{chem}}$ (determined using a bond order cutoff of 0.3 for counting bonds).

<table>
<thead>
<tr>
<th>Structure</th>
<th>GaSb</th>
<th>GaSb$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{\text{Ga-Ga}}$</td>
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<td>2.47</td>
</tr>
<tr>
<td>$r_{\text{Ga-Sb}}$</td>
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<td>$N_{\text{chem}}^{\text{Sb-Sb}}$</td>
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<td>2.91</td>
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</table>

The structure factors $S(Q)$ (figure 5) differ only slightly for AD and MQ for both compositions. For GaSb, the most notable difference is the shape of the first sharp diffraction peak (FSDP) at 0.75 Å$^{-1}$ in the $S(Q)$ with neutron scattering weights. This is related to intermediate range correlations. The calculated peak positions in $S(Q)$ (1.94, 3.21 Å$^{-1}$ (AD), 1.93, 3.19 Å$^{-1}$ (MQ)) are in satisfactory agreement with the XRD values (1.87, 3.19 Å$^{-1}$) [31]. The most obvious change for GaSb$_7$ is also in the FSDP region (near 1 Å$^{-1}$). In the AD structure, there are small maxima at 0.75 and 1.25 Å$^{-1}$ in the neutron and x-ray $S(Q)$, while for MQ there is a shoulder at 1–1.25 Å$^{-1}$ in the neutron $S(Q)$ and only slight modulation in the x-ray $S(Q)$ for MQ. At higher $Q$, the AD and MQ structures are very similar.

3.2. Bond angle distributions

The bond angle distributions for GaSb are shown in figure 6. The main peaks for Ga-centred configurations and Ga–Sb–Ga are near the tetrahedral value (109.5$^\circ$), while the Sb–Sb–Sb and Ga–Sb–Sb angles lie between the tetrahedral and octahedral (90$^\circ$) values. The Sb configuration is mainly fourfold coordinated, and further analysis shows that 72% of Sb are tetrahedral in MQ. A number of Ga atoms form three-membered rings, because there are peaks near 60$^\circ$ for Ga–Ga–Ga and Ga–Ga–Sb. These peaks remain after MQ, and inspection of the structure shows that three-membered rings (triangles, see figure 4(a)) form clusters ranging from a rhombus formed by two triangles (four atoms) to a chain with up to ~15 atoms, all of which participate in triangular configurations.

The bond angle distributions for GaSb$_7$ are shown in figure 7. All Sb-centred angles lie between octahedral (90$^\circ$) and tetrahedral (109.5$^\circ$) values, while Ga-centred configurations are centred around the tetrahedral bond angle.
Figure 6. Bond angle distributions in GaSb for (a) Sb–Sb–Sb, (b) Ga–Sb–Sb, (c) Ga–Sb–Ga, (d) Ga–Ga–Ga, (e) Ga–Ga–Sb and (f) Sb–Ga–Sb bonds (cutoff 3.2 Å). Red: AD, blue: MQ. Dashed vertical lines at tetrahedral angle (109.5°) and (c)–(e) 60°.

Table 2. Nearest neighbour composition (at.%, for configurations with >2%) for amorphous GaSb and GaSb$_7$ using a chemical bond order cutoff of 0.3 for counting bonds. The total weight for a particular coordination is given in boldface.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Coordination</th>
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<td>MQ</td>
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Figure 7. Bond angle distributions for GaSb\(_7\). Notation as in figure 6.

Figure 8. Ring sizes in amorphous GaSb and GaSb\(_7\). The bond cutoff is 3.2 Å.

3.3. Ring size distributions

The distributions of ring sizes are shown in figure 8, which shows that rings with five (AD) and six (MQ) atoms dominate in GaSb. Triangular configurations occur, and the absence of rings with more than eight members in both structures indicates the absence of the large cavities found in other phase change materials [14, 36]. The total cavity volumes are 22% (AD) and 20% (MQ), and the larger cavity domains [5] in AD indicate a different surface-to-volume ratio.

The variations in ring sizes are smaller in GaSb\(_7\) than in GaSb; five-membered rings are the most common, and—unlike GaSb—there are rings with more than eight atoms. This is consistent with the smaller total coordination for Sb (more free space) and with the presence of larger individual cavities enclosed by large rings. The total cavity volumes are 24% (AD) and 22% (MQ). The smaller cavity domains in the MQ structure indicate a higher cavity surface-to-volume ratio for AD, as in GaSb.

3.4. Electronic densities of states, bond orders

The electronic densities of states (DOS) were calculated for the final structures of GaSb and GaSb\(_7\) and are shown for the MQ structures in figure 9. The differences in the MQ DOS for the two lower s-bands reflect the different chemical compositions; the lower band is associated with Sb, the higher with Ga. The calculated band gaps (GaSb: 0.15 eV, GaSb\(_7\): 0.13 eV) probably underestimate the optical gaps. The inverse participation ratio (figure 9) is a measure of the localization of individual wavefunctions. The lower energy bands are more localized (especially the Ga s-band in GaSb\(_7\) at −6 eV), but

(Ga–Ga–Ga statistics are limited). This is reflected in the total coordination numbers for Ga (∼4) and Sb (∼3), where the latter differs from GaSb with a significantly smaller number of tetrahedral configurations (19% in MQ). The total coordination numbers for both species change little from AD and MQ. Triangular configurations (bond angles ∼60°, figure 4(d)) are less common in GaSb\(_7\) than in amorphous GaSb, and they are much less common after MQ. They should not be viewed as intrinsic features of the amorphous structure.
Figure 9. Electronic densities of states (DOS, black, states eV$^{-1}$) for MQ GaSb and GaSb$_7$ (red: s-component, blue: p-component). Grey: inverse participation ratio (IPR, right scale). DOS were plotted with a Gaussian broadening ($\sigma = 0.03$ eV for each state).

there is also increased localization at the band edges near the Fermi energy.

The chemical bond orders (figure 10) are mainly between 0.6 and 0.9 (a covalent single bond has the value 1), and the weaker bonds are due to increased 'metallicity' for Ga and Sb. Sb–Sb bonds are the strongest. There are shoulders and intermediate maxima between the main peak (bonds) and nonbonded distances (zero strength), as seen in the Ga–Ga distributions for GaSb and GaSb$_7$ (AD) and the Ga–Sb distributions for GaSb$_7$ (both AD and MQ). The small maximum in the GaSb$_7$ (AD) bond strengths for Ga–Ga bonds at 0.4 is from a single bond only, and it is visible because there are very few Ga–Ga bonds in the structure.

The sharp bond order cutoff (0.3) means that some bonds are not counted, even if they are shorter than the corresponding $r_{\text{min}}$. This can lead to smaller than expected coordination numbers. Some Ga atoms with ‘threelfold’ coordination have other bonds with order less than the cutoff, and the tendency for threefold-coordinated Sb atoms to have bond angles near 90° indicates that octahedral structures (3+3) are favoured, as in bulk Sb.

The details for the Ga–Sb bond strengths in GaSb$_7$ are interesting. There are local maxima (arrows in figures 10(c) and (d), Ga–Sb curve) near 0.6, and the atom pairs participating in these bonds are often two tetrahedrally coordinated atoms with one bond to the partner atom and the other three to Sb atoms. Atom pairs also form five-membered rings with three other atoms, with the ring path proceeding via the bond between the atom pair (see figure 11(a)). The fourfold coordination favoured by the Sb atoms in these pairs (AD: 93%, MQ: 97%) is much larger than usual (AD: 14.9%, MQ: 17.5% for all Sb). The Sb atoms forming such bonds then comprise a significant fraction (~40%) of the total number of fourfold-coordinated Sb atoms. Over 90% of Ga atoms are fourfold coordinated in both AD and MQ structures.

3.5. Segregation and clusters

We noted in section 1 that phase separation is an important consideration in Ga/Sb alloys, and our GaSb$_7$ structures show small Sb-rich domains with diameters of the order of 1 nm. As in our previous studies of Ge in Ge$_{15}$Te$_{85}$ [7, 36], we have computed the fraction of Sb atoms that do not coordinate with Ga, and we find 61–62% for AD and MQ samples. The ‘empty’ regions in figure 12 represent segregation, since there are no Sb atoms that are bound to Ga atoms.

Some clusters of Ga atoms in GaSb (AD) (nine Ga atoms and one Sb atom, figure 11(b)) are reminiscent of crystalline Ga. Eight Ga atoms form a planar ribbon, and the remaining atoms have perpendicular bonds to it. This cluster is more planar than the corresponding structure for crystalline Ga and has two fewer atoms, one neighbour from each of the sixfold-coordinated Ga atoms (‘hub’ atoms, red dots). The bond orders of this cluster showed that the longer bonds (2.78–2.89 Å, bond strength 0.22–0.28, green in figure 11(b)) connecting four atom pairs across the ribbon are weaker than the shorter bonds along the ribbon (2.48–2.57 Å, bond strength 0.52–0.61, marked blue in figure 11(b)). We have shown the corresponding bonds in the c-Ga structure using similar colours. The three diagonal bonds within the ribbon are close to the former and have bond lengths (strengths) of 2.66 Å (0.36), 2.55 Å (0.44), and 2.81 Å (0.25), respectively.

The MQ procedure eliminates this cluster, but a similar one is found in the final MQ configuration for GaSb (figure 11(c)). This cluster has two Ga ‘hub’ atoms 2.78 Å apart, each of which has four Ga neighbours (of which two are shared and one is the other hub) and one Sb neighbour within 3.03 Å. The hub atoms in the MQ cluster are initially tetrahedrally coordinated in the AD GaSb structure, indicating that the cluster in MQ GaSb is formed during MQ from atoms that were ‘normal’ in AD GaSb.

4. Concluding remarks

We have simulated the as-deposited (AD) and melt-quenched (MQ) structures for amorphous GaSb and GaSb$_7$ phase change materials. Bulk AD samples with 528 atoms were formed by depositing sparse layers of atoms sequentially on a fixed template at 300 K and compressing the structure to the appropriate densities. Melt-quenched (MQ) samples were then produced by heating these structures above the melting point and quenching. These calculations demonstrate
Figure 10. Chemical bond strengths (orders) for GaSb and GaSb$_7$. The arrows mark local maxima at 0.6 corresponding to fourfold Sb.

Figure 11. Structural details for MQ GaSb$_7$ (a) and for GaSb ((c) AD, (b) MQ) similar to crystalline Ga (d). In (a) tetrahedrally coordinated Ga and Sb atoms (centre) form two linked five-membered rings and a six-membered ring including Sb. Red dots: hub atoms, white dots: partner atoms in Ga dimers (in (d)), blue and green lines: intermediate bonds (in (b), marked as reference in (d)), black: long bonds (in (c), 3.03 Å each). Orange: Ga, purple: Sb.

again the ability of DF/MD calculations to simulate the ‘as-deposited’ structures relevant to many experiments. The crucial aspect of AD is that deposition does not lead to a liquid phase with high atomic mobility, and the local atomic environment evolves from low coordination due to interfacial growth. The calculated structure factors and pair distribution functions for GaSb agree well with XRD measurements on deposited GaSb films [31].

In GaSb, both elements prefer tetrahedral coordination, there are numerous five- and sixfold rings that are more
common in the MQ structure, and threefold rings in the AD and MQ structures form atomic arrangements similar to crystalline Ga. GaSb$_7$ shows a fourfold coordination for Ga and threefold coordination for Sb, with Sb bond angles between octahedral and tetrahedral values. As in AIST alloys [14], the Sb coordination can be characterized as 3+3 defective octahedral with short and long bonds. It has been proposed for AIST that a concerted bond interchange mechanism around each Sb (‘avalanche’) is responsible for the rapid crystallization [14], and the same argument applies to GaSb$_7$. Five- and six-membered rings are common in GaSb$_7$, but the AD and MQ distributions are similar, and the existence of larger rings indicates a different topological disorder from GaSb.

Ga and Sb atoms become more interconnected during MQ, leading to fewer homopolar bonds and little change in the average coordination numbers. The absence of homopolar bonds in crystalline GaSb is consistent with the more rapid crystallization of the MQ structure [17]. The ring distributions peak at five- and six-membered rings in both alloys, and cavities make up ~20–24% of the total volume. Melt-quenching the AD structure reduces the cavity volume slightly for both structures, but the effect is larger for the shapes and volumes of individual cavities. The lack of rings with more than eight atoms in GaSb is consistent with few cavities, and there are larger rings in GaSb$_7$.

The possibility of segregation in Sb-rich alloys of Ga and Sb is important for their application in PC materials, and the GaSb$_7$ structures show small Sb-rich domains of the order of 1 nm diameter. Phase separation is possible in such films, but atomistic studies of this effect would require the simulation of much larger systems than are currently possible using DF/MD calculations. We also found cluster-like structures in GaSb that are reminiscent of the crystalline structure of Ga. We emphasize that the present calculations were computationally extremely demanding, but the structures found should provide a sound basis for planned simulations of other Ga$_x$Sb$_{1-x}$ alloys.

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