A theoretical approach to modeling the amorphous phase of GeTe for PCM

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ABSTRACT

We present a theoretical investigation of amorphous GeTe (a-GeTe), in which the a-GeTe structures were generated via a classical potential and then characterized via density-functional-theory calculations. With this dual approach, we were able to produce a sufficiently large number of configurations to provide a statistic of defects. We identified which defects are mainly responsible for localized states in the electronic band gap. We propose that, over time, there is a reduction of these states related to the consumption of defects formed during the fast quenching. Our model shows that this reduction results from a slow evolution of the bond network towards lower-energy structures having a first-neighbor topology more similar to that of the crystalline phase. We suggest that this evolution is responsible for the change in resistivity of the amorphous phase observed in the experiments.

Key words: molecular-dynamics simulations, first-principles simulations, defects in a-GeTe, resistance drift

1. Introduction

Phase-change materials (PCM) based on chalcogenide alloys are considered very promising for memory storage applications. These materials are interesting because they undergo fast and reversible transitions between the amorphous and crystalline phases upon heating and cooling. These two phases have different electrical resistivities, which can be used to store and read the information. To render PCM-based devices competitive with flash memories, the amount of data that can be stored per unit of volume must be increased by setting more than two resistance values in the same cell. Unfortunately, the main limitation incurred hereby is data corruption caused by a change in resistivity of the amorphous phase on a timescale that is too short for a practical storage application. This limitation becomes even more relevant when trying to store more resistance values. Therefore, understanding the cause of the resistivity drift is a key step forward towards plan solutions to increase the storage density.

This study focuses on the amorphous phase of GeTe, a prototypical PCM material currently being explored for memory applications. The goal is to investigate whether changes in resistivity are associated with a reorganization of the bond network in the amorphous phase or with the evolution of specific defects formed during the relatively fast quenching from the melt in the writing cycle. We used first-principles methods based on density-functional theory (DFT) to characterize the electronic properties of a large number of a-GeTe structures generated via the classical Tersoff-based potential. To produce a-GeTe structures, we preferred the classical potential over DFT because of the long time, on the order of tens of nanoseconds, necessary to quench liquid GeTe to the amorphous phase. This work focuses entirely on the DFT analysis carried out on a-GeTe.

2. Method

As mentioned above, we used both DFT and classical calculations. We generate a-GeTe structure using molecular dynamics (MD) and replica-exchange (RE) simulations using the classical potential we built via the fit parameters of the augmented Tersoff potential (described in Ref. [1]) plus additional parameters [2] to reduce the mismatch with the forces and the energies of relevant GeTe structures precomputed via DFT simulations. We quenched l-GeTe from 985 K to room temperature (RT) at constant density with different quenching rates. Additional a-GeTe structures were selected from configurations corresponding to the lowest temperatures in the RE simulations. We used different system sizes (up to 1000 atoms) and different densities. Selected structures obtained at RT via the classical potential

were subsequently optimized via DFT PBE calculations using the CPMD code [3-4]. Here we describe the analysis of 73 structures consisting of 108 GeTe units optimized at 5.65 g/cm^3. We determined the topology of the bond network using localized Wannier orbitals instead of a distance criteria. The electronic density of states and optical conductivity were computed using both PBE and HSE functionals, the latter served to improve the description of the band gap. We defined a parameter to compare the conductivity of the structures. This parameter was defined as the integral of the optical conductivity, defined by the Kubo–Greenwod formula, over a selected range of energies. We use this parameter to sort and group the configurations from more to less resistive. The averages were carried out over the structures of each group.

3. Results

The main advantage of this study is that a relatively large number of structures was analyzed, so that we were able to average over more configurations to find correlation between the structure of the bond network and the electron properties. First, we identified that most of defects, about 55%, responsible for electronic states localized in the band gap are produced by groups of Ge atoms, not necessary covalently bonded, but closer than 2.8 Å, in which at least one Ge atom is over- or under-coordinated, two examples are reported in Figure 1a. We also identified other three types of defects present in lower concentrations, about 5% each. They are made close cubes not properly aligned (see Figure 1b), four-fold coordinated Ge atoms (see Figure 1c), and pairs of Te atoms at distances lower than 4 Å most of the times associated to close cubes not properly aligned.

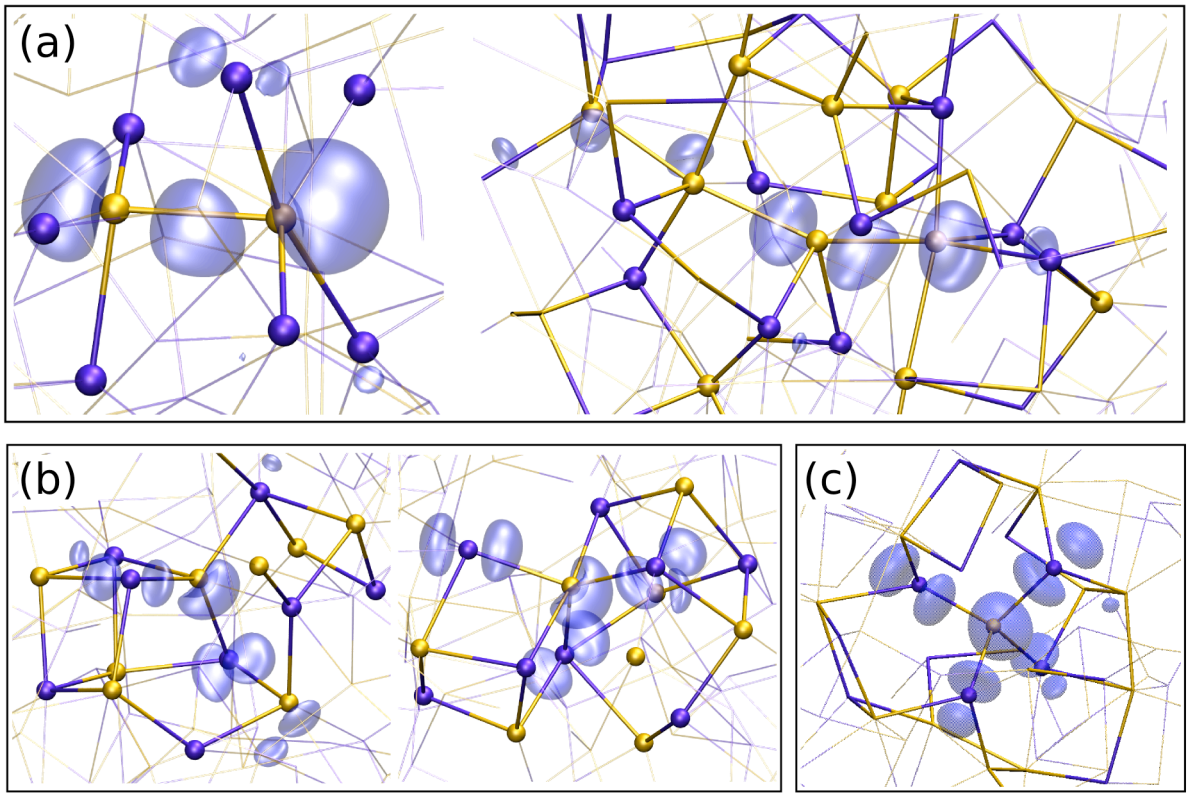

Figure 1. Structures responsible of localized states in the band gap. Ge and Te atoms are depicted in yellow and blue, respectively. The Kohn-Sham states are indicated by a blue contour plot.

Second, we used the integrated optical conductivity (cf. Sec. 2) to describe how resistive a configuration is compared with the others. We found that more resistive geometries present the following structural features; (i) a lower fraction

of Ge–Ge bonds (about 2.4% of the total number of Wannier orbitals) is present in the more resistive structures, than in the more conductive ones (4%), cf Table 1. (ii) More resistive structures have a higher fraction of unstrained Ge–Te bonds with a bond length between 2.70–2.85 Å, a center of charge located at 30–40% along the Ge–Te bond closer to the Te atom, and with both Ge and Te three-fold coordinated and one lone pair for each, as in crystalline GeTe. These unstrained bonds are indicated via the label "good" in Table 1. (iii) More resistive structures have a smaller number of groups of Ge atoms containing over-/under-coordinated atoms.

	% of bonds			% of lone pairs (lp)		Ge[3+1]-Te[3+1]	Ge[4+0,4+1]-Te[3+1]
	Ge-Ge	Ge-Te ("good")	Te-Te	lp-Ge	lp-Te		Ge[5+0,5+1]-Te[3+1]
higher resistivity ↑	2.4	57.1 (34.1)	0.3	17.7	22.6	31.5	10.2
	2.6	57.1 (33.2)	0.2	17.4	22.7	29.2	10.9
	2.8	57.3 (32.2)	0.2	17.3	22.5	29.0	12.4
	2.9	57.2 (30.9)	0.2	17.2	22.6	27.2	12.0
	3.1	56.6 (30.4)	0.3	17.0	23.0	25.0	13.0
	4.1	56.2 (29.6)	0.3	16.0	23.4	24.0	14.8

Table 1. Analysis of the fraction (in percentage) of double occupied orbitals involved in Ge–Ge, Ge–Te and Te–Te bonds, and lone pairs on Ge and Te atoms. We use the notation [3+1] to indicate that an atom is three-fold coordinated and has one lone pair.

4. Conclusions

The main finding of this analysis is that most of the states localized in the electronic band gap are associated with the presence of structures meeting mainly two requirements: i) they contain Ge atoms at distances shorter than 2.8 Å but not necessary connected by a direct covalent Ge–Ge bond; ii) at least one of the Ge atom has to have a coordination that differs from that of the crystalline phase (three bonds and one lone pair). We propose that these defects formed during the fast quenching can slowly evolve into lower-energy structures with a larger number of Ge–Te bonds with a topology more similar to that of the crystalline phase. To support this model, structures with a smaller number of Ge–Ge bonds have been created via classical MD simulations using an artificially modified potential. These structures on average exhibit a larger gap and less localized states in the band gap. A detailed analysis of all the states localized in the band gap is currently being performed to identify whether there are exceptions to this rule, and whether also other effects should be taken into account to improve the reliability of the model. What are the implications? If this model captures at least part of the causes of the resistivity drift, a solution aimed at preventing the reconstruction of the bond network could be to increase the rigidity of the amorphous network by doping with atoms that can make stronger covalent bonds. Steps in this direction have been already propose by Beneventi *et al.* in [5], in which they report of a reduced drift produced by carbon-doped GeTe.

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