Tersoff-based potential for amorphous GeTe

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ABSTRACT

We present a density functional theory study of amorphous GeTe in which the amorphous structures are generated via a new classical potential constructed to reproduce *ab initio* forces and energies. In this work we describe the methodology used to develop the classical potential and its application to the study of defects in a-GeTe.

Key words: molecular-dynamics simulations, first-principles simulations, augmented Tersoff potential

1. Introduction

Phase-change materials (PCM) based on chalcogenide alloys are considered very promising candidates for memory storage applications, because they undergo fast and reversible transitions between the amorphous and the crystalline phase upon heating. These two phases have different electrical and optical properties, and this is exploited to store data. Currently, the main limitation is data corruption due to a change in electrical resistivity over time in the amorphous phase. Our focus is on the binary amorphous GeTe (a-GeTe), which we choose as prototypical system. The ultimate goal of this work is to find what causes the drift in resistivity; in particular, we investigate whether changes in resistivity are associated to a release of stress of the amorphous network or to the presence of specific defects formed during the relatively fast quenching from the melt in the writing cycle. In this study, we aim to find out whether there are defects that produce localized states close to the Fermi energy that could affect the electronic properties of the system.

A realistic model of a-GeTe requires long molecular-dynamics (MD) simulations to quench large samples from the melt whose size is large enough to avoid possible interactions introduced artificially by the use of periodic boundary conditions. Because first-principles (FP) MD simulations cannot address nanosecond time scales of systems consisting of hundreds of atoms efficiently, we use a dual approach based on both classical MD and FP calculations. The idea is to use classical MD simulations to generate amorphous structures that will then be characterized by means of FP calculations. In this work, we present the methodology used to develop a new classical potential for GeTe and its application to the study of defects in a-GeTe.

2. Method

The classical potential is built via the fit parameters of the augmented Tersoff potential (described in Ref. [1]) to reproduce the forces and the energies of relevant GeTe structures precomputed via FP simulations.

First, we generate the reference structures using FP Car-Parrinello [2] and Born-Oppenheimer simulations based on density functional theory (DFT) using the PBE approximation [3] and the CPMD code [4]. MD simulations at $T = 1200$ K are used to generate a liquid structure (l-GeTe), then the temperature is reduced to room temperature at rates on the order of hundreds of Kelvin per picoseconds to produce a-GeTe. Additional structures are taken from snapshots of MD simulations of crystalline GeTe (c-GeTe) at temperatures below 600 K. To introduce vacancies, we remove selected atoms from c-GeTe.

Then, the parameters of the potential are updated to minimize the energy and the force mismatch simultaneously. During the optimization, additional structures are produced with the classical potential and post-processed with the DFT method to increase our database. The DFT equation of state of the crystalline phase, the pair correlation functions, and the angle distributions of liquid and amorphous GeTe are well reproduced.

3. Results

Different a-GeTe configurations are produced via classical MD simulations at densities ranging from 5.65 to 6.39 g/cm^3 around the experimental value of 5.95 g/cm^3 under the same conditions as in the experiment, namely, by quenching the system in 4 ns and 10 ns from 985 K to room temperature to generate a-GeTe and c-GeTe, respectively.
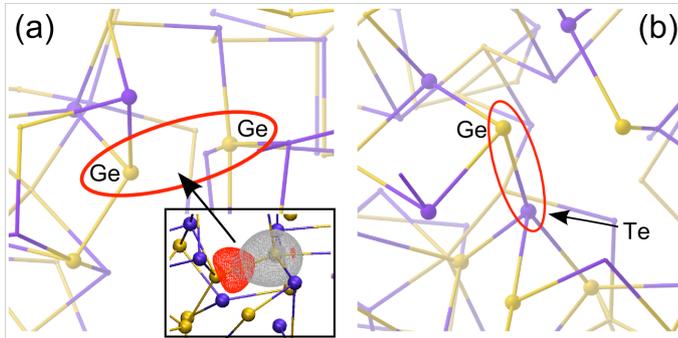
The amorphous structures are characterized by DFT calculations. Localized Wannier functions are used to identify lone pairs and bonds as well as to investigate whether there is a link between particular local structures and the electronic density of states near the Fermi energy (E_F). Among several tens of configurations consisting of 3000 GeTe units, we identified two unique defects localized in space and at energies close to E_F, see the figure below. In particular, in panel **(a)** two lone pairs localized on Ge atoms point towards each other, and in panel **(b)** there is a strained Ge-Te bond, in which the Te atom is overcoordinated (four-fold coordinated). The contour plots in the inset of panel **(a)** show the isosurfaces of the Wannier functions of the two lone pairs.

4. Conclusions

We present a theoretical study of a-GeTe, in which the amorphous structures are obtained via classical molecular dynamics simulations and then characterized via first principles methods. The methodology we use in this work allows the modeling of a-GeTe via classical MD simulations and the identification of localized defects via FP calculations. A relatively small concentration of defects (about one per every 10^3 GeTe units) localized near the Fermi energy is found. We are currently increasing the number of amorphous configurations to find other possible defects, to estimate their concentration, and to analyze the effect of the resistivity.

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Biographies

Dr. **Federico Zipoli** is a Research Staff Member at IBM Research – Zurich since 2011. He graduated in Materials Science at the University of Milano-Bicocca, Milan, Italy, in 2003, and obtained his Ph.D in Nanostructures and Nanotechnology in 2006, also in Milan. He is an expert in molecular-dynamics simulations, in first-principles calculations of electronic and structural properties of condensed systems, and in the study of chemical reactions and diffusion processes at surfaces of silicon and silica. At IBM, his current research topic is phase-change materials for storage applications (the argument of this presentation).

Dr. **Alessandro Curioni** heads the Mathematical and Computational Sciences Department at IBM Research – Zurich, and is a member of the IBM Academy of Technology. He received his diploma in Theoretical Chemistry and his PhD in Computational Materials Science from the Scuola Normale Superiore, Pisa, Italy. He joined IBM Research – Zurich in 1998 as Research Staff Member in the Computational Biochemistry and Materials Science Group. Since then he has developed and applied advanced computational methods to the study of materials issues related to IBM's core and exploratory technologies and to the investigation of important molecular processes in life sciences. He is an expert in high-performance computing and a major developer of the highly popular CPMD code.