

Large scale molecular dynamics simulation of the crystallization of GeTe at the crystal-amorphous interface

Giacomo Miceli, Gabriele C. Sosso, Marco Bernasconi

Department of Materials Science, University of Milano-Bicocca, Milano, Italy

Sebastiano Caravati

Computational Science, Department of Chemistry and Applied Biosciences, ETH Zurich, and Facoltà di Informatica, Istituto di Scienze Computazionali, Università della Svizzera Italiana, Lugano, Switzerland

Jörg Behler

Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Bochum, Germany

ABSTRACT

We simulated the crystallization of amorphous GeTe in contact with the crystalline phase by means of molecular dynamics and a classical interatomic potential generated by fitting a huge ab-initio database with a Neural Network method. The potential has a close-to-ab-initio accuracy and allows simulating thousands of atoms for tens of ns at an affordable computational cost. The simulations provided an estimate of the speed of crystal growth of 5.5 m/s at 500 K in the most favorable conditions under which the density is dynamically adjusted during the crystallization process. The crystallization speed is reduced by a factor three by constraining the density of the amorphous phase to that of the crystal, mimicking the operation conditions of the memory cells.

Key words: molecular dynamics simulations, crystallization, GeTe

1. INTRODUCTION

The detailed mechanism of the crystallization process of phase change materials is actively investigated experimentally and theoretically because of its relevance for applications in data storage. The direct simulation of this process by molecular dynamics techniques holds the promise to shed light on the peculiar features that make some chalcogenide alloys suitable to undergo crystallization in the time scale of 10-100 ns. Some examples of simulations based on density functional theory have already been reported albeit with still very small simulation cells [1]. To overcome the limitations in cell size and simulation time of density functional molecular dynamics, we have recently developed a classical potential for GeTe by fitting a huge database of density functional energies by means of a Neural Network (NN) method [2]. The potential allows us to simulate several thousands of atoms for several nanoseconds.

In this work, we applied the NN potential to study the crystallization of the amorphous phase of GeTe at the amorphous-crystal interface. We repeated the simulations at different densities of the amorphous phase aiming at clarifying the effect of pressure on the crystallization speed. This is of relevance for phase change memory cells as in the current mushroom geometry the amorphous region is produced upon melting of a small droplet of crystalline material inside a polycrystalline film. The density of the amorphous phase is thus constrained by the surrounding polycrystalline material resulting in a compressive stress. It was indeed shown experimentally that the crystallization temperature of thin Ge₂Sb₂Te₅ films encapsulated between cladding layers increases with respect to that of free films due to the compressive stress exerted from the encapsulation material [3]. The simulations discussed hereafter allowed us to estimate the speed of crystal growth and its dependence on the density of the amorphous phase.

2. COMPUTATIONAL METHODS

The classical interatomic potential of GeTe was obtained by fitting a huge database of density functional energies by means of the Neural Network (NN) method introduced by Behler and Parrinello [4]. As discussed in Ref. [2], the NN potential was developed by fitting the total energies of about 30000 configurations of 64-, 96-, and 216-atom supercells computed by employing the the Perdew-Burke-Ernzerhof (PBE) exchange and correlation functional and norm conserving pseudopotentials. The NN potential displays an accuracy close to that of the underlying DFT-PBE framework whose reliability in describing structural and dynamical properties of GeTe and other phase change materials has been validated in several previous works by us [5,6] and other groups [1,7]. The generation of the NN potential and the NN molecular dynamics simulations were performed with the code RuNNer [8]. Although the generation of the NN potential is computationally very demanding due to the very large number of ab-initio reference calculations, systems as large 4000 atoms can then be easily studied with a computational load five order of magnitude lower than that of an equivalent density functional calculation. The simulation of a 4096-atom cell takes 1.5 min/ps on a 256 cores of a Cray XT5 computer.

3. RESULTS & DISCUSSION

To study the crystallization dynamics we first had to assess the ability of the NN potential and thus of the DFT-PBE framework to reproduce the melting temperature. We computed the melting temperature of GeTe by means of thermodynamic integration [9] and a cubic 4096-atom supercell. We first computed the difference in the Helmholtz free energy F between the NN system and a reference system for which an analytic expression for F is known, namely $F_{NN} - F_{ref} = \int_0^1 d\lambda \langle U(\lambda) \rangle$, where $U(\lambda) = \lambda U_{NN} - (\lambda-1)U_{ref}$ and the average is taken over a MD simulation with the interatomic potential $U(\lambda)$. This was done at constant volume and at the temperature $T_0=998$ K corresponding to the experimental values at the melting point at normal conditions [10]. The reference system was chosen as an Einstein crystal for the solid and a Lennard-Jones fluid for the liquid. The pressure-volume equation of state at fixed temperature was then computed to obtain from F the chemical potential at constant pressure and temperature. By equating the chemical potential of the two phases one obtains the transition pressure at the chosen temperature T_0 . From the calculated Clausius-Clapeyron equation ($dT/dP=6.85$ K/GPa from the calculated ΔS and ΔV on the melting line at $T=998$ K) we then obtained the theoretical melting temperature at normal pressure of $T_m=1001$ K, very close to the experimental value. It turned out that in order to reproduce the equation of state of the liquid, an empirical van der Waals (vdW) correction had to be added to the NN potential. This was done by using the scheme proposed by Grimme [11] with the s_6 parameter tuned to reproduce the experimental equilibrium volume of the liquid [10]. The added vdW interaction acts just as a volume dependent term in the equation of state but it is not included in the molecular dynamics simulations discussed below. From the equation of state we then obtained the thermal expansion coefficients of the liquid and amorphous phases in good agreement with experimental data of liquid GeTe [10] and in line with the experimental values available for the amorphous phase of other materials in this class [otherexp]. However, the addition of the vdW interaction leads to an overestimation of the density of the amorphous by as much as 10 %. This misfit might also originate from an experimental overestimation of the density of the liquid on which the vdW interaction has been tuned to. Nevertheless, from the intersection of the volume versus temperature curves of the two phases computed with the same vdW interaction, we can obtain a consistent estimate of the glass transition temperature [13] of $T_g=505$ K, close to the values measured experimentally for GeSbTe alloys by means of differential scanning calorimetry [14]. This theoretical value of the glass transition temperature is, however, subject to large uncertainties.

We then simulated the crystallization of amorphous GeTe in contact with crystalline GeTe in the superlattice geometry shown in Fig.1. We generated the amorphous slabs by quenching from the melt by first fixing the crystalline atoms and then allowing them to relax. The resulting model consists of 2592 atoms in the amorphous slab and 1152 atoms in the crystalline slab. We considered two models, one with the amorphous at its theoretical equilibrium density and a second with the amorphous constrained at the density of the cubic crystal. This is of interest because in memory devices operation the amorphous spot is embedded in the crystalline phase and therefore its density is constrained by the surrounding. The calculated pressure of the amorphous region generated at the density of the crystal is 0.2 GPa which is of the order of 10 % of the pressure expected from the bulk modulus of the amorphous and the difference in

equilibrium density between the amorphous and the crystal. This occurs because the amorphous generated under pressure from the liquid phase is able to accommodate the constraint on the density in a much more efficient way than a model generated at the equilibrium density of the amorphous and then pressurized to obtain the density of the crystal at room temperature.

For the amorphous model at its equilibrium density, we also performed two different simulations: one with the density of the overall model fixed and a second with the density adjusted during the crystallization process in such a way that the amorphous and the crystalline slabs were always at their equilibrium density. This is achieved by classifying the atoms as belonging to the crystal or to the amorphous with a variant of the q_6 local order parameter for crystallinity [15]. The temperature was then raised to 500 K and the evolution of the system monitored for 850 ps. In Fig.1 we report the final configuration of the system with the density fixed at that of the crystal or adjusted dynamically. The crystallization speed can be estimated by visual inspection of the atomic trajectories, by counting the number of crystalline planes formed as a function of time. The crystal growth is layer-by-layer from the crystal-amorphous interface with a finite roughness. The crystallization speed in the most favourable situation with the density dynamically adjusted is 5.5 m/s, close to the values recently measured experimentally in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ by ultrafast differential scanning calorimetry [16]. The crystallization speed turns out to be 3 times slower when the density of the amorphous is constrained at the density of the crystal.

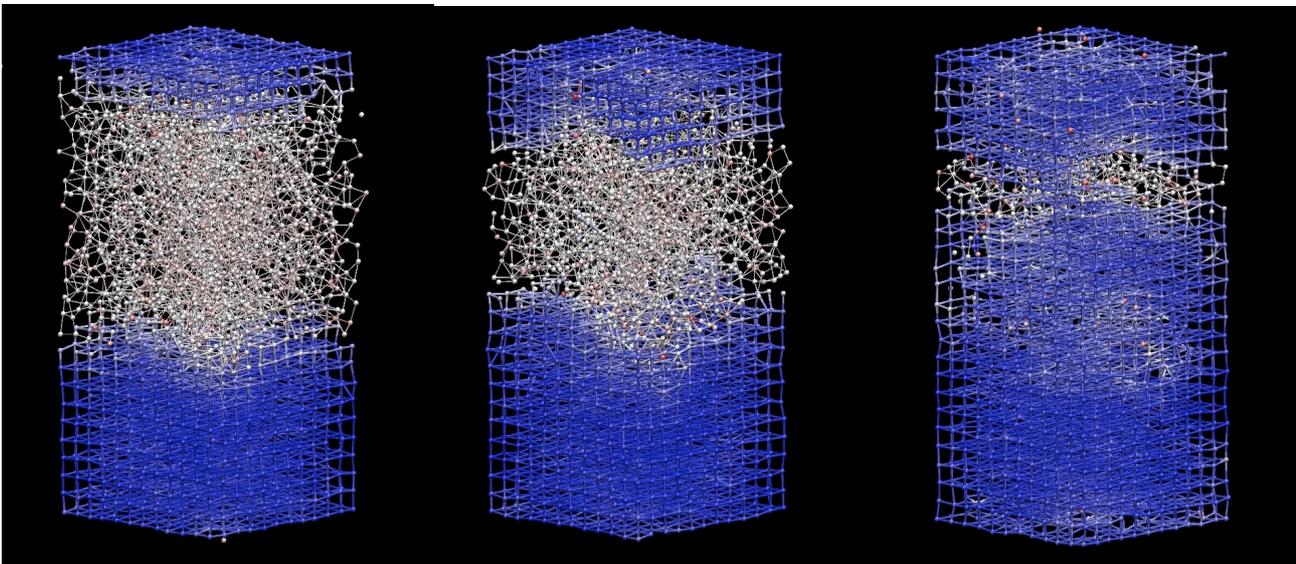


FIGURE 1. Left panel: initial configuration of the slab used to simulate the crystallization of amorphous GeTe in contact with the crystalline cubic phase. The atoms depicted in blue are crystal-like (see text). The final configurations after 850 ps at 500 K of the system with the amorphous phase at the density of the crystal or dynamically adjusted during crystallization are shown in the central and right panels.

4. CONCLUSION

We simulated the crystallization process of amorphous GeTe in contact with the crystalline phase by means of large scale molecular dynamics. We employed a recently devised classical interatomic potential for GeTe generated by the fitting of a huge database of DFT energies by means of a Neural Network technique [2]. The simulations of several thousands of atoms allowed us to estimate the crystallization speed for different densities of the amorphous phase. The crystallization speed at 500 K is 5.5. m/s, close to the values recently measured for GST by ultrafast DSC [16], when the density is adjusted dynamically during the simulation in such a way that the amorphous and crystalline part of the slab are always at their equilibrium density. The crystallization speed is reduced by a factor three for an initial configuration with the amorphous generated at the density of the crystal and by holding fixed the overall density of the model. Our results confirm that the volume constraint due to the surrounding crystalline phase in memory devices is expected to reduce the crystallization rate with respect to the values measured in free films.

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Biographies

Marco Bernasconi received the undergraduate degree in Physics at the University of Milano in 1988 and the Phd in Theoretical Condensed Matter Physics at Sissa (Trieste) in 1993. He spent two years as a postdoc at the Max-Planck-Institut für Festkörperforschung (Stuttgart, Germany) in the group of Prof. M. Parrinello and then joined the Department of Materials Science of the University of Milano-Bicocca (Milano, Italy) where he holds the position of associate professor in Condensed Matter Physics since 2001. His research activity is devoted to the ab-initio modelling of materials ranging from amorphous semiconductors and insulators for applications in microelectronic and photonics to fast ion conductors and low-Z superconductors. He is author of 107 articles on international journals among which 12 deal with phase change materials.