

***Ab initio* Molecular-dynamics Simulation of Crystal Nucleation in GST**

S.R. Elliott and T.H. Lee
Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, UK
(srel@cam.ac.uk; thl32@cam.ac.uk)

ABSTRACT

We report the results of *ab initio* simulations of the crystallization of amorphous GST, concentrating particularly on the early stages of the crystallization process, i.e. the nucleation. The stochastic nature of the homogeneous nucleation in this material is demonstrated, and the size of the critical nucleus size has been estimated for the first time. The structural ordering around the critical nuclei has been analysed, and such structural configurations explain why the crystallization is so fast, in terms of the very low interfacial energy at the crystal nucleus-amorphous interface estimated from the simulations. The crystal growth rate estimated from the simulations is in very good agreement with the experimental value extrapolated to the simulation temperature.

1. INTRODUCTION

Although phase-change (PC) materials, such as Ge-Sb-Te (GST), have been used as non-volatile memory materials for many years in optical data storage, and more recently in electronic PCRAM applications, nevertheless certain aspects of the PC process remain unclear – notably why is the crystallization so fast (~10 ns) in these materials. In particular, little is known about the crystal-nucleation process, and such information is extremely difficult to obtain experimentally. Thus, computer simulation can play a very important role here. It is now possible to perform *ab initio* molecular-dynamics (AIMD) simulations for long enough times (~ ns) and for large enough systems (~ 2nm) in order to capture this nucleation behaviour for the first time [1]. We report here the first such study of crystal nucleation in GST.

2. METHOD

We have performed constant-volume AIMD simulations of Ge₂Sb₂Te₅ using the Vienna *Ab initio* Simulation Package (VASP) code. Three 180-atom models were independently quenched to 300K from a liquid at 1073K to form glasses, and then crystallized by annealing at a temperature (600K) intermediate between the glass-transition and crystal-melting temperatures.

3. RESULTS & DISCUSSION

All 3 GST models crystallized to the metastable rocksalt structure on annealing at 600K. Such crystallization exhibited a stochastic distribution of onset times (i.e. 70ps, 190ps, and 270ps), as

observed in experiments [2] and assumed in classical nucleation theory (CNT) [3]. Three distinct phases in the crystallization process can be distinguished: I, an incubation period during which $(\text{Ge,Sb})_2\text{Te}_2$ 4-rings constantly form and disappear, a small proportion of which also form transient layered structures comprising the rings and also isolated $(\text{Ge,Sb})_4\text{Te}_4$ cubes; II, a period in which locally ordered layer structures and the number of cubes start to grow, and at the end of which a critical nucleus of connected cubes is formed; III, a period in which the crystal grows outwards from the nucleus. The critical nucleus size found from these simulations for annealing at 600K is a cluster comprising ~ 7 cubes. If this cluster size corresponds to the actual critical-nucleus size, the interfacial energy between the metastable rocksalt phase of GST and the amorphous phase, calculated from CNT, is $\sim 5 \text{ mJ/m}^2$; that is approximately an order of magnitude smaller than that between the hexagonal and liquid phases of GST (40 mJ/m^2) [4]. The (logarithm) of the crystal-growth rate found for all 3 simulations has the average value $\ln u(\text{pm/s}) = 29.3$, which compares very favourably with values in the range 24-29 extrapolated to $T = 600\text{K}$ from the experimental growth data for GST (i.e.. an activation energy of $2.35 \pm 0.05 \text{ eV}$ [5]).

The most significant features found during the crystallization process are: i) formation of a cluster of cubes of atoms in the region of an ordered planar structure; ii) growth of that cluster, preceded by growth of a layer of planes at the interface. Such behavior was not observed for transient structural units in the incubation period I. It can be speculated that the interfacial energy between the crystal cluster and the surrounding amorphous phase is significantly reduced due to the presence of the shell of planes (having the same bond orientation as that of the cluster of cubes) at the interface, thereby facilitating crystallization. The interfacial energy between the metastable rocksalt and amorphous phases of GST is also expected to be anomalously small because of the very similar (defective) octahedral atomic coordination in both solid phases of this material, consistent with the low interfacial energy described previously. It should be emphasized that, in GST, this is possible because the average bond angles are all $\sim 90^\circ$, which facilitates the formation of the intermediate structure.

CONCLUSIONS

Ab initio molecular-dynamics simulations of the thermally induced crystallization of the phase-change memory material GST have provided the first estimate for the critical crystal-nucleus size, viz. ~ 7 $(\text{Ge,Sb})_4\text{Te}_4$ cubes. The simulated crystal-growth rate is in good agreement with the experimental value extrapolated to the simulated annealing temperature (600K).

REFERENCES

1. J. Hegedus and S. R. Elliott, *Nat. Mater.* **7**, 399 (2008)
2. B.-S. Lee et al., *Science* **326**, 980 (2009).
3. K. F. Kelton and A. L. Greer, 'Nucleation in Condensed Matter: Applications in Materials and Biology' (Elsevier, Oxford, 2010), p. 279-329.
4. J. A. Kalb, F. Spaepen, and M. Wuttig, *J. Appl. Phys.* **98**, 054910 (2005).
5. J. Kalb, F. Spaepen, and M. Wuttig, *Appl. Phys. Lett.* **84**, 5240 (2004).

BIOGRAPHY

Stephen Elliott is Professor of Chemical Physics and Head of the Chemical Physics Group (<http://www-cpg.ch.cam.ac.uk/>) in the Department of Chemistry at the University of Cambridge, and a Professorial Fellow at Trinity College, Cambridge.