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Classical-nucleation-theory analysis of priming in chalcogenide phase-change memory

Jiri Orava ^{a, b, *}, A. Lindsay Greer ^{a, b, **}^a Department of Materials Science & Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, United Kingdom^b WPI Advanced Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

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ABSTRACT

The chalcogenide $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) is of interest for use in phase-change memory. Crystallization is the rate-limiting step for memory operation, and can be accelerated by the prior application of a “priming” heating pulse. There is characteristic fading of the priming effect if there is a time interval between the priming pulse and the main heating pulse to achieve crystallization. We apply classical nucleation theory to interpret these effects, based on a fitting of nucleation kinetics (steady-state and transient) over the full temperature range of the supercooled liquid. The input data come from both physical experiments and atomistic simulations. Prior studies of conventional glass-formers such as lithium disilicate preclude any possibility of fading; the present study shows, however, that fading can be expected with the particular thermodynamic parameters relevant for GST and, possibly, other phase-change chalcogenides. We also use the nucleation analysis to highlight the distinction between GST and the other archetypical chalcogenide system (Ag,In)-doped Sb_2Te . Classical nucleation theory appears to be applicable to phase-change chalcogenides, and to predict performance consistent with that of actual memory cells. Nucleation modeling may therefore be useful in optimizing materials selection and performance in device applications.

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1. Introduction

Chalcogenide phase-change (PC) materials, exemplified by $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) and (Ag,In)-doped Sb_2Te (AIST), have been widely studied for their use in optical (DVD, Blu-ray™) and electrical (phase-change random-access memory, PC-RAM) data recording [1]. These applications exploit the high contrast in reflectance and resistance upon reversible glass-to-crystal transitions. Recent interest has included such applications as display and data visualization [2], and synaptic switching [3]. In the case of PC-RAM, a relatively low-power electrical pulse heats the glassy chalcogenide above its glass-transition temperature, T_g , crystallizing it (SET operation). The reverse switching is achieved by heating the crystal with a relatively short high-power pulse above its melting temperature, T_m , and subsequent rapid quenching (at 10^9 – 10^{11} K s^{-1} [4,5]) of the liquid into the glassy state (RESET operation).

Crystallization is of particular interest as the SET operation is the rate-limiting step for memory switching. At and just below their melting temperatures, the PC chalcogenide liquids have low viscosities [6–11], similar to those of liquid pure metals [12]; the consequent high molecular mobility allows the SET times to be short (of order 1–10 ns). Even so, for PC-RAM in particular, there are ongoing efforts to shorten the crystallization time and also to reduce the energy needed to switch between memory states.

Early kinetics studies showed that differences in the crystallization rates of glassy GST samples are largely due to differences in the kinetics of crystal nucleation [13]. In isothermal annealing, there is an incubation time before the onset of crystallization, and this time is temperature-dependent [13]. In GST, the incubation time is much shorter in melt-quenched than in as-deposited amorphous films, and this was attributed to a population of quenched-in crystallites [13,14]. The generation of such crystallites is a priming effect [15]. Priming is of interest in several contexts [16–18], but the present interest in priming of phase-change memory (PCM) has been driven by the work of Loke et al. [19], who showed that applying a constant low voltage ahead of the SET pulse (Fig. 1) could reduce the crystallization time from 5 ns to 0.5 ns. This dramatic acceleration was attributed to ‘pre-structural

* Corresponding author. University of Cambridge, United Kingdom.

** Corresponding author. University of Cambridge, United Kingdom.

E-mail addresses: jo316@cam.ac.uk, orava.jiri@gmail.com (J. Orava), alg13@cam.ac.uk (A.L. Greer).

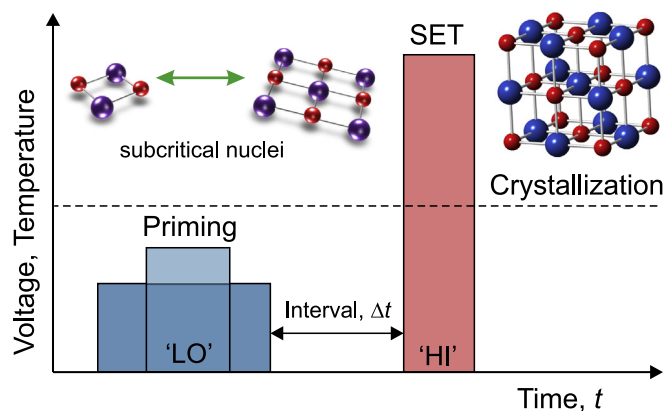


Fig. 1. In the operation of PC-RAM, a high-power (HI) ‘SET’ electrical pulse is used to heat an amorphous chalcogenide causing it to crystallize. The application of a prior low-power (LO) priming pulse can reduce the total time and energy involved in crystallization [18,19]. In priming, a variety of combinations of pulse length and power have been used, with or without the interval Δt . The atomic configurations illustrate schematically that priming works by generating subcritical crystalline clusters that aid the nucleation of the ultimate crystalline structure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ordering’, interpreted as a growth in the population of subcritical crystalline nuclei (clusters) in the amorphous phase.

In an idealized glass devoid of subcritical crystalline clusters, annealing at a given temperature leads to a cluster size distribution with populations increasing with time until they reach a steady-state distribution characteristic of the anneal temperature. The evolution of the cluster size distribution in glasses was first modeled in detail by Kelton et al. [20] to understand the origin of the incubation time in the context of classical nucleation theory (CNT). Their rate-equation analysis showed that a pre-existing distribution of clusters can shorten the effective time-lag for nucleation. Focusing first on thermodynamic and kinetic parameters typical for an oxide glass (lithium disilicate, LS_2) and later on metallic glasses, Kelton and Greer showed that numerical modeling of transient size distributions could be useful in understanding glass-forming ability and in validating the kinetic model in CNT [21–23].

Modeling of this type was first extended to a chalcogenide (GST) by Senkader and Wright [24], who used it successfully to fit the incubation time results mentioned above [13]. They noted that the crystallization of a PCM cell takes place entirely in a transient nucleation regime [24].

For PC chalcogenides (in contrast to the lack of work on other amorphous systems) there have been several microscopical studies of cluster distributions. These have been based on fluctuation transmission electron microscopy (FTEM), permitting statistical detection of nanoscale ordering, attributable to subcritical clusters. While the absolute size distribution cannot be precisely determined, relative changes can be reliably inferred [25]. Comparing cluster size distributions in GST and AIST in various states, it is found that:

- subcritical size distributions can be detected and can be altered by annealing, laser treatment or melt-quenching [26];
- pre-existing larger (smaller) cluster populations are associated with shorter (longer) nucleation incubation times [25–27];
- annealing effects (larger population, shorter incubation) saturate when the steady-state cluster size distribution is established [25];

- in GST melt-quenching gives more and larger clusters than in the as-deposited state, and this effect is greater on slower quenching [28];
- in AIST melt-quenching gives fewer and smaller clusters [27];
- the characteristic behaviors of GST and AIST are readily distinguished [27];
- N-doping effects in GST can be interpreted in terms of nucleation kinetics [29].

These microscopical observations are complemented (i) by kinetic (rate-equation) studies [24,30] and (ii) by atomistic simulations of ordering and the onset of crystallization in liquid chalcogenides [19,31–35]. Together, these studies provide support for interpretations of phase-change kinetics based on classical models of crystal nucleation and growth. These studies have focused on crystallization kinetics within the volume of the amorphous chalcogenide. Given the small volume of PCM cells, there has to be concern about surface and interface effects, particularly on crystal nucleation. Nevertheless, many studies suggest that there is a wide range of conditions under which surface and interface effects can be ignored [13], especially in the absence of oxidation [36].

We use CNT to examine the evolution of crystalline cluster size distributions, especially to explain priming effects in GST. There are many reasons for interest in multiple-pulse interactions, including the parallel writing of memory arrays [18] and the possibility of undesirable *read-disturb* [37], but our immediate focus is on improving SET switching. Lee et al. showed that the use of prior priming pulses can reduce not only the duration of the SET pulse necessary for switching (as shown earlier [19]), but also the total pulse duration and the total energy. That is: the total duration of the priming and shortened SET pulses is shorter (by up to 33%) than the duration of the SET pulse that would be necessary without priming, and similarly for the total energy (up to 43% less) [18].

Classical analyses of crystallization kinetics show that the rates of both nucleation and growth show a maximum as a function of temperature between T_g and T_m , and that the maximum in nucleation rate occurs at significantly lower temperature than that for growth. These maxima are exploited in two-stage heat treatments to control the microstructural development in devitrification of oxide glasses, the first, lower-temperature treatment being used to obtain the desired population of nuclei, and the second, higher-temperature treatment being used to grow crystallites to the desired size. As noted in several works [18,19,34], the priming treatment and the SET pulse applied to PC chalcogenides can be considered analogous to these two stages, and, if so, priming should be best achieved in the temperature range of the maximum in nucleation rate.

If there is an interval Δt in which no current is applied, between the priming pulse and the SET pulse (Fig. 1), the effect of the priming pulse fades (substantially, but not totally), with a relaxation time of $\sim 1 \mu\text{s}$ [18]. Lee et al. considered possible electrical and thermal effects to explain why the required SET pulse length increases with increasing Δt after the priming pulse, but they concluded that the *fading* must be intrinsic to the chalcogenide material (Ref. [18], Suppl. Info.). In general, it is considered that priming and switching effects in PCM are purely thermal, arising from Joule heating [38].

As shown schematically [18], during the priming pulse a subcritical cluster size distribution develops and increases towards the steady-state distribution for the temperature established during the pulse. At the end of the priming pulse, the temperature drops, and the cluster size distribution, if it changes at all, must evolve towards the steady-state distribution characteristic of a

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