Chalcogenides for Phase-Change Memory Applications

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Chalcogenide phase-change (PC) materials, exemplified by Ge$_2$Sb$_2$Te$_5$ (GST) and (Ag,In)-doped Sb$_2$Te$_3$ (AIST), have been widely studied for their use in optical (DVD, Blu-ray™) and electrical (phase-change random-access memory, PC-RAM) data recording. More recently, displays and synaptic switches, exploiting respectively the high contrast in reflectance and resistance upon reversible glass-to-crystal transitions, have been attracting increasing attention. In the case of PC-RAM, a single long and low-power electrical pulse heats the glass above its glass-transition temperature, $T_g$, crystallizing it, which is a rate-limiting step of the memory operation taking <100 ns (Fig. 1). Glass is obtained by heating the crystal with short and high-power pulse and consequent rapid quenching of the liquid (critical cooling rates $10^8$–$10^{11}$ K s$^{-1}$).

For the memory to be commercially successful, several conflicting requirements must be met. Focus of the talk is mainly on crystallization, which must be fast, but the glass should not crystallize spontaneously at elevated temperatures. This requirement can be met by the presence of a fragile-to-strong crossover on cooling the liquid [1,2]. The glass should also not undergo structural relaxations, which would for example influence the intermediate states during long-term depression in synaptic switching.

While there is on-going research to find the ‘best-performance’ composition, priming of the supercooled liquid (Fig. 2), in other words a pre-structural ordering by an auxiliary pulse before the main crystallization voltage (SET), has been shown to be a promising alternative in reducing crystallization times to less than $10^{-9}$ s [3].

We will discuss a theoretical description of pre-bias priming. While priming may look contradicting the classical nucleation theory (CNT) from studies of silicate-based glasses, it can be shown that priming can be well described in terms of CNT with the particular thermodynamic properties of PC chalcogenides. An attempt is made to link crystallization kinetics from atomistic simulations and experiments using thermodynamic and time-dependent CNT descriptions. Two chalcogenide PC systems are considered, each with distinct input parameters for the temperature-dependent viscosity in the calculations of transient and steady-state nucleation rates. Firstly, GST is taken to exemplify a high-fragility liquid with crystal growth partly decoupled from viscosity. Secondly, the influence of a fragile-to-strong crossover on crystallization will be considered in liquid AIST. We also hint on the origin of fading of such effect, i.e. the priming effects relaxes when there is an unbiased period between the auxiliary and the main pulse.
We may show that photocrystallization, at temperatures which are just a fraction of $T_g$, a reversible growth of crystalline phase, which may be difficult to obtain by traditional thermal annealing from supercooled liquid, can be induced. This is unlike the thermal crystallization in optical disks (CD-RW, DVD), where alike in PC-RAM the glass is heated with a laser above its $T_g$ to crystallize it, and above its $T_m$ to amorphize it.

Understanding and controlling the temperature dependence of atomic mobility, i.e. the kinetic term in nucleation and crystal-growth rates, can pave the way for trimming the PC-RAM switching times to less than 1 ns, ultimately leading to devices that are more power-efficient.

Fig. 1  Schematic of the phase-change processes in PCM and optical disk media with the corresponding atomic arrangements ($T_x$ is the crystallization temperature, and $T_m$ is the melting temperature).

Fig. 2  Schematic of a pre-bias priming in PC-RAM. A variety of combinations of pulse lengths and powers have been used, with or without a delay time, $\Delta t$, which is the period without any applied bias. ‘LO’ and ‘HI’ stand for low- and high-power pulses, respectively.

