



Statistics of crystallization kinetics in nanoscale systems

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We investigate the statistics of the crystallization kinetics caused by the finite size of nanoscale samples. We define a characteristic length, L_C , as a function of the material properties, in order to describe the sample size dependence of the statistics. We find that the samples smaller than L_C undergo single-nucleus crystallization, which yields wide distributions of the half-transition time. Finally, we apply our theory to find a way to improve the data retention statistics of sub-20 nm phase-change memory.

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The crystallization of an amorphous phase lowers the total free energy of the system. The Johnson–Mehl–Avrami–Kolmogorov (JMAK) equation is a standard equation for crystallization kinetics, yielding an “S-curve” for the transformed fraction as a function of time, $X(t)$ [1–3]:

$$X(t) = 1 - \exp(-bt^n) \quad (1)$$

The parameters are $b = (1/3)\pi V_G^3 I_N$ and $n = 4$ for an infinitely large 3-D sample with a constant average nucleation rate, I_N , and a constant growth velocity, V_G . One may note that Eq. (1) is deterministic and thus does not yield any statistical deviation of $t_{0.5}$, the half-transition time. There have been a number of theoretical studies on non-JMAK systems, such as nonisothermal nucleation and growth, anisotropic growth of nuclei, surface or grain-boundary nucleation, and variable growth velocity [4–9]. Some researchers have presented analytical models for finite size samples where there are only a few nuclei and the crystallization kinetics is slightly slower than the JMAK model [10,11]. Zhang and Banfield [12] presented experimental data and a model on the crystallization kinetics of an array of titania nanoparticles that deviates from the JMAK

equation. However, none of them presented statistical fluctuation of crystallization time or a quantitative criterion for the onset of finite size effects, although it is obvious that the more fluctuation, the smaller the sample.

Recently, such statistics have become increasingly important in sub-20 nm phase-change memory (PCM), which adopts confined cells, as shown in Figure 1 [13]. The PCM is the most promising nonvolatile memory (NVM), which uses reversible transition (or phase change) between crystalline and amorphous states (data 0 and 1) of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST225), thanks to its excellent scalability and reliability compared to other NVMs [14–16]. Its data retention, the most important requirement for NVMs, is directly related to the crystallization kinetics. It is known that the retention times of a PCM array have a log-normal distribution [17]. More importantly, the data retention times are longer but more widely distributed in smaller cells [18,19]. The tail bits of the higher density memory with more than 10^9 bits (cells) may produce critical problems.

In this report, we present our simulation results on $t_{0.5}$ distribution for sub-10 nm cells and propose an analytical model on the crystallization kinetics of extremely small cells. In addition, we suggest a way for material engineering to improve the tail-bit retention. We believe that our findings are of great importance in both industry and academia. GST225 is known as a system

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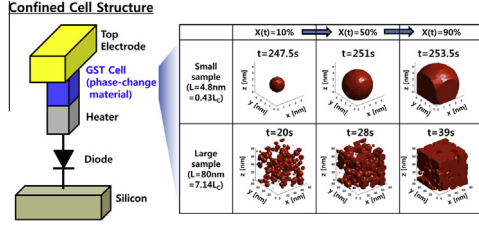


Figure 1. The confined GST225 cell structure for sub-20 nm technology is demonstrated on the left [13]. The crystallizations of a small cell and a large cell at 190 °C are shown on the right. These are snapshots from our PFM simulations.

where isotropic homogeneous nucleation is dominant [20]. Its nucleation rates and growth velocities are known as a function of temperature [21,22]. The anisotropy is not high, as shown in atomic force microscopy images by Kalb et al. [23]. Weinberg and Birnie [5,11] showed that small anisotropy does not alter the standard JMAK kinetics. Therefore, we accept all JMAK assumptions except the finite size.

We define a characteristic length, L_C , as a criterion of the finite size effects. Let us consider a cubic sample with an edge length of L . The average time interval between nucleations is $\tau_N = (I_N L^3)^{-1}$. The average growth time for one nucleus to crystallize the entire cube is $\tau_G = 1.315L/V_G$ where the $1.315L$ is the average interfacial moving distance to complete the crystallization of the sample. The ratio of τ_G to τ_N is determined by the sample size, L , if I_N and V_G are given.

$$\frac{\tau_G}{\tau_N} = \frac{1.315L^4}{V_G/I_N} = \left(\frac{L}{L_C}\right)^{1/4} \quad (2)$$

where $L_C = (V_G/1.315V_G)^{1/4}$. We obtain $L_C = 10.5$ nm for our GST225 at our retention test temperature (190 °C), where $I_N = 2.60 \times 10^{-5} \text{ nm}^{-3} \text{ s}^{-1}$ and $V_G = 0.41 \text{ nm s}^{-1}$ [19].

Weinberg also used the ratio of the nucleation rate to the growth velocity without presenting any further quantitative meaning [10]. Hereafter, we focus on 190 °C retention.

One can expect that in a very small sample, with $L \ll L_C$ (equivalently, $\tau_G \ll \tau_N$), it takes a long time for one nucleus to appear and the crystallization completes by the growth of the first nucleus before the second nucleus appears. The crystallization time is determined by the occurrence of the first nucleus which is distributed over time. Let us call this regime single nucleus crystallization (SNC). Conversely, in a large sample with $L \gg L_C$ (equivalently, $\tau_G \gg \tau_N$), many nuclei will form, which results in little deviation in $t_{0.5}$, corresponding to the standard JMAK kinetics. The two extreme cases of $L = 4.8$ nm and $L = 80$ nm are demonstrated in Figure 1. There may be three regimes of the crystallization such as the SNC, the intermediate, and the JMAK regimes. We perform simulations for a range of cell sizes in order to reveal a more quantitative relation between the relative cell size (L/L_C) and the crystallization regime.

We use the phase-field method (PFM). The main variable in the PFM is the order parameter, $(\eta(\vec{r}))$, related to local crystallinity in our case. The $(\eta(\vec{r}))$ is also called phase-field because $(\eta(\vec{r}))$ indicates a material phase that

is crystalline (zero) or amorphous (one). The $(\eta(\vec{r}))$ must vary smoothly over interface regions to ensure the numerical stability. The time evolution of $(\eta(\vec{r}))$ proceeds in the direction of reducing the total energy of the system, which comprises the bulk free energies and the interfacial free energy, as described by the Allen–Cahn equation [24]:

$$\frac{\partial \eta}{\partial t} = -L_\eta \left[\frac{df(\eta)}{d\eta} - \kappa \nabla^2 \eta \right] \quad (3)$$

where $f(\eta)$ is a local free energy density function having two minima, at $\eta = 0$ (crystal) and $\eta = 1$ (amorphous).

$$f(\eta) = \frac{W}{4} \eta^2 (\eta - 1)^2 + \eta^3 (10 - 15\eta + 6\eta^2) \Delta G \quad (4)$$

At 190 °C, the parameters of Eq. (3) and (4) are $L_\eta = 2.31 \times 10^{-9} \text{ m}^3 \text{ J}^{-1} \text{ s}^{-1}$, $\kappa = 2.16 \times 10^{-11} \text{ J m}^{-1}$, $W = 1.28 \times 10^9 \text{ J m}^{-3}$ and $\Delta G = 2.00 \times 10^8 \text{ J m}^{-3}$. Our choice of parameters yields the interfacial energy of $\gamma = \int_0^1 \sqrt{2\kappa f(\eta)} d\eta = 68.8 \text{ mJm}^{-2}$, which lies within the literature values (40–100 mJ m^{-2}) [22,25,26]. Our calibration is based on the measurement data from Samsung’s 58 nm PCM sample. Further details are presented in our previous report [19].

Eq. (3) is solved by obtaining the finite difference ($\Delta x = 0.4$ nm) with reflective boundary conditions. Simulation starts from the initial condition that the entire GST225 is amorphous ($\eta(\vec{r}) = 1$ everywhere). The probability that one nucleation occurs during a small time step ($\Delta t \ll 1$) is calculated from the following equation:

$$P = 1 - \exp[-I_N \Omega_A(t) \Delta t] \quad (5)$$

The exponential term represents the probability of no nucleation during Δt , and thus P represents the probability of one nucleation during $t \sim t + \Delta t$. The $\Omega_A(t)$ is the volume of the amorphous (uncrystallized) region that is a function of time. The probability that the first nucleation occurs during $0 \sim t$ is $P(t) = 1 - \exp(-t/\tau_N)$ because $\Omega_A(t=0) = L^3$. If nucleation is determined to occur during Δt , then a location within the amorphous region is selected randomly. The Δt is maintained to be small enough to be $I_N \Omega_A(t) \Delta t \ll 1$, as well as to maintain the numerical stability. This type of nucleation supply is called Poisson seeding [8].

All simulation results are summarized in Table 1. As the cell size decreases, the average half-transition time, $\bar{t}_{0.5}$, becomes larger, which is consistent with prior observations [18,27]. As the cell size increases, the $\bar{t}_{0.5}$ converges to 27.0 s, which is 9.3% larger than the JMAK value (24.7 s). This is because the PFM simulation implicitly

Table 1. Summary of simulation results.

L [nm]	$\bar{t}_{0.5}$ ($\pm\sigma$)	Occurrence of nucleations	Number of samples
160	27.0 (± 0.2)	2743.6 (± 56.4)	50
80	27.4 (± 0.6)	354.9 (± 14.8)	1000
40	28.3 (± 1.6)	46.9 (± 5.4)	1000
20	31.3 (± 6.6)	6.6 (± 2.0)	1000
14.8	35.2 (± 12.2)	2.9 (± 1.2)	1000
10	56.4 (± 39.0)	1.4 (± 0.6)	1000
6.8	127.9 (± 111.1)	1.1 (± 0.3)	10,000
4.8	357.2 (± 352.2)	1.0 (± 0.1)	10,000

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