Kinetics of electric field enhanced crystallisation in phase-change materials

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Abstract. We study the effect of electric field on crystallisation kinetics in phase change materials within the framework of classical nucleation theory. We identify the parameter set where the electric field has a pronounced effect on the crystallisation of phase-change materials.

1. Introduction
Phase change materials have a unique combination of structural, electronic, and optical properties [1]. The amorphous and crystalline states are both stable at room temperature and exhibit a large difference in optical reflectivity and electrical resistance. At the same time the transition between the two phases can be achieved on very short timescales. These properties make phase-change materials suitable for a wide range of electrical applications including various optical and electrical memories. Well known phase-change materials are based on chalcogenide alloy systems, such as Ge-Sb-Te, Ag-In-Sb-Te, and In-Sb-Te [2]. In present phase-change materials are also considered for future emerging technologies, such as Probe-based Terabit Memory (ProTeM) [3] or for use in phase-change random access memory (PCRAM).

Crystallisation of phase-change materials is often modelled at the continuum level either using the Johnson-Mehl-Avrami-Kolmogorov (JMAK) approach or models based on separable nucleation and growth models. Unfortunately many of the assumptions on which JMAK formalism is based are violated in real switching events in phase-change devices. The approach based on nucleation and growth models deals with crystal clusters at or above the critical nucleus size. More sophisticated models based on rate equations should be used to study the role of sub-critical clusters [4]. Nevertheless, the simple nucleation and growth model has been successfully employed for a wide variety of problems [5,6,7]. An alternative to these continuum models is the cellular automata model developed by Wright et al [8], which uses the Gillespie algorithm to determine the outcome of a Monte Carlo simulation. More recently ab initio atomic scale models based on density functional theory have been used to model the crystallisation of phase-change materials [9].

In this paper, we use the nucleation switching model [7] to study the kinetics of crystallisation of phase-change materials. In the nucleation switching model the nucleation of amorphous materials is dependent on the applied electric field. Using the nucleation model we identify the parameter set where the electric field has a pronounced effect on the crystallisation of phase-change materials. The paper is organized as follows. In the next section we give a brief summary of the thermodynamics and kinetics of electric field enhanced crystallisation. In section 3, we present the crystallisation properties
of phase-change material Ge-Sb-Te when the electric field is present. In particular, we discuss the crystallisation times at various temperatures and electric fields. The paper finishes with conclusions in section 4.

2. Electric field enhanced crystallisation

Crystallisation of phase-change materials enhanced by electric field has been recently studied by Karpov et al [7]. According to this work the nucleation rate is dependent of the applied voltage and the idea of field enhanced nucleation of a shunting crystalline cylinder has been put forward. In this model the initial crystalline clusters appear to be spherical and assumed to be highly conductive and therefore their induced dipole moment interact with the field, decreasing the system energy and thus facilitating nucleation. According to this scenario when the electric field is present the switching continues with the nucleation of a long \((h \gg R)\) conductive cylinder that acts as a “lightning rod” concentrating the electric field. The stronger electric field facilitates nucleation of an additional conductive particle at the cylinder end making it longer and hence further increasing the field.

A nucleated “metal” particle changes the local electric field strength \(E\) and decreases the electrostatic energy [7]

\[
E = E_0/n \quad \text{and} \quad W_E = -0.5\varepsilon E^2/n
\]  

where \(\varepsilon = \varepsilon_r \varepsilon_0\) with \(\varepsilon_r\) is the relative electric permittivity and \(\varepsilon_0\) is permittivity of free space. The depolarising factor is \(n = 1/3\) for a spherical particle, and for a long cylinder it takes the form of

\[
n = (R/h)^3 \left[ \ln (2h/R) - 1 \right].
\]

2.1. Thermodynamics

2.1.1. Spherical particle. The classical nucleation theory derived for condensed systems assumes that formation of a spherical cluster of new phase requires a free energy \(G\) given by

\[
G = A_{sph} \sigma - V_{sph} g
\]

where \(A_{sph} = 4\pi R^2\) and \(V_{sph} = 4\pi R^3/3\) are the surface and volume of the spherical cluster with radius \(R\), and \(\sigma\) is the surface energy. The bulk free energy difference \(g\) between the amorphous and crystalline phases is considered to be temperature dependent. In this paper we use the form established by Peng et al. [5]

\[
g = g(T) = \begin{cases} 
H_2 \left[ 1 - \frac{T}{T_g} \left( 1 - \frac{H_1}{H_2} \frac{T_m - T_g}{T_m} \right) \right] & \text{if } T \leq T_g \\
H_1 \frac{T_m - T}{T_m} & \text{otherwise}
\end{cases}
\]

but other slightly different forms are also known in the literature (see for example, [4,6]). The corresponding parameter values are listed in table 1. Minimising \(G\) gives the critical radius \(R_0\) and nucleation barrier \(W_0\) of a spherical particle

\[
R_0 = 2\sigma/g(T) \quad \text{and} \quad W_0 = 16\pi\sigma^3/3[g(T)]^2.
\]

and the temperature dependence of these parameters is illustrated in figure 1.
Figure 1. Critical nucleus radius and the corresponding nucleation barrier as function of the temperature according to Eq. (5).

The electric field modifies the free energy $G$ (see equation (3)) and in case of a spherical particle it obeys the form of

$$G_{sph} = A_{sph} \sigma - V_{sph} [g(T) + g_{sph}(E)],$$

with $g_{sph}(E) = 1.5 eE^2$ using $W_E$ in Eq. (1) and $n = 1/3$ for a spherical particle. Therefore, the electric field decreases both the critical radius and nucleation barrier when the field is large according to

$$R_{sph} = 2\sigma/[g(T) + g_{sph}(E)] \text{ and } W_{sph} = 16\pi\sigma^3/3[g(T) + g_{sph}(E)].$$

This dependence is demonstrated in figure 2.

Figure 2. Electric field dependence of the critical radius and nucleation barrier according to Eq. (7).

2.1.2. Cylindrical particle. The free energy for a cylindrical particle is given by

$$G_{cyl} = A_{cyl} \sigma - V_{cyl} [g(T) + g_{cyl}(E)],$$

with $A_{cyl} = 2\pi Rh + 2\pi R^2$, $V_{cyl} = \pi R^2 h$ and $g_{cyl}(E) = 0.5 eE^2 (h/R)^2$, where following [7] we have neglected the logarithmic dependence in Eq.(2). The corresponding nucleation barrier normalised to $W_0$ as a function of cylinder radius $R$ and length $h$ (normalised to $R_0$) is shown in figure 3.
In nucleation theory the surface and volume energy terms have physical meanings if the cylindrical particle has a minimum radius $R_{\text{min}} = \alpha R_0$. Following the work in reference [7], we are using $\alpha = 0.1$ throughout this paper. The nucleation barrier for a cylindrical shaped particle can be lower than the corresponding nucleation barrier of a spherical particle (the latter would approximately correspond to ‘coordinates’ of $(R = R_0, h = 2R_0)$ in figure 3). It can be shown that the relevant energy barrier for crystallisation along the line $R_{\text{min}} = \alpha R_0$ is lowered compared to spherical particles according to

$$W_{\text{cyl}} = 1.5W_0 \left[ \alpha^2 + \left( \frac{2}{3\sqrt{\pi}} \right) \left( \alpha - \alpha^2 \right)^{3/2} \left( E_0 / E \right) \right], \quad (9)$$

as illustrated in figure 4. The characteristic field $E_0$ is defined to be equal to $E_0 = \sqrt{W_0 / \varepsilon R_0^3}$.

**Figure 3.** Surface and contour plots of the normalised nucleation barrier for cylindrical particles.

**Figure 4.** Reduction of the nucleation barrier for cylindrical particle with minimum radius $R_{\text{min}} = \alpha R_0$ according to equation (9).

### 2.2. Kinetics

The crystallisation kinetics of phase-change materials has been extensively studied by various groups for various applications [1]. It is common in all these calculations based on the nucleation theory, as described in section 2.1, that crystallisation occurs either by the nucleation of critical size particles and...
their subsequent growth within the untransformed region (homogeneous nucleation), or by the growth of crystallites at the boundary between the untransformed region and the surrounding crystalline matrix (heterogeneous nucleation). In this paper we only consider the first scenario as no specific geometry for the phase-change material is taken into account, although following [5,6], the phase-change layer is assumed to have been discretised into cells of \( \Delta = 1\ \text{nm}^3 \) in this work. The probability of an untransformed cell in the amorphous state to be become crystalline during the time interval \( dt \) is given by

\[
P = \nu \cdot dt \cdot \exp[-\beta (E_a + W)],
\]

where \( \nu \) is a frequency factor related to atomic vibrations, \( \beta = 1/k_B T \) where \( k_B \) is the Boltzmann constant, \( E_a \) is the activation energy associated with nucleation and \( W \) is the nucleation barrier.

### Table 1. Parameters used in this study.

| Symbol | Value | Unit | Ref |
|--------|-------|------|-----|
| \( H_1 \) | 418.9 | J/cm\(^3\) | 5 |
| \( H_2 \) | 218.9 | J/cm\(^3\) | 5 |
| \( T_m \) | 889 | K | 5 |
| \( T_g \) | 673 | K | 5 |
| \( \sigma \) | 0.033 | J/m\(^2\) | 10 |
| \( \nu \) | 4E+25 | Hz | 5 |
| \( E_a \) | 2.19 | eV | 5 |
| \( \varepsilon_r \) | 10 | | 7 |

### 3. Results and discussion

We follow the crystallisation of the amorphous material by calculating the time evolution of the crystalline fraction given by

\[
\chi(t) = \chi(t - dt) + P[1 - \chi(t - dt)].
\]

Each simulation was performed at constant temperature and constant electric field starting from an initially amorphous sample (e.g. \( \chi(t = 0) = 0 \)).

#### 3.1. Spherical particles

The crystallisation map depicts the required crystallisation times for the amorphous sample to fully crystallise (e.g. \( \chi = 1 \)) at a given temperature and electric field. For spherical particles the effect of the electric field is negligible at low fields below \( E < 10^7\ \text{V/m} \), as seen in figure 5. At these low fields the temperature has the dominant effect and the optimal crystallisation time can be achieved for the temperature range between 650 and 700K according to figure 5. Below 400K and above 800K the crystallisation times can be orders of magnitude longer than for the optimised temperature range.

At larger electric fields (e.g above \( E > 10^8\ \text{V/m} \)), the field has a pronounced effect and reduces the crystallisation time. According to the results shown in figure 5 the electric field significantly enhances crystallisation speed by about two to three orders of magnitude (if keeping temperature constant but changing only the electric field).

Theoretical predictions for emerging probe storage applications [11] have shown that within these devices it is not uncommon to see high electric fields of up to \( E \sim 10^8\ \text{V/m} \). Therefore, in principle, crystallisation of spherical particles in probe storage devices can be enhanced by the electric field.
Nevertheless, we show below in section 3.2 that for cylindrical shaped particles the crystallisation time can be further reduced at even lower fields.

![Figure 5](image1.png)

**Figure 5.** Crystallisation times for spherical particle at different temperatures and electric fields.

### 3.2 Cylindrical particles

The crystallisation times of cylindrical shaped particles may be smaller in comparison to spherical shaped particles due to lower nucleation barrier, as described in section 2.2. We have therefore repeated the calculations in section 3.1 using the free energy term in equation (8). We found that at low electric fields below $E < 10^7$ V/m the crystallisation times are much larger for cylindrical shaped particles than for the spherical particles, as shown in figure 6. On the other hand for large fields above $E > 10^8$ V/m the crystallisation times appear to be very similar both for spherical and cylindrical particles.

The crystallisation times for cylindrical particles is reduced in the ‘transition regime’ for fields between $10^7$ V/m $< E < 10^8$ V/m, as shown in figure 6. It can be seen that there is a much wider optimal temperature range for the crystallisation times. For example, it emerges from figure 5 that the optimal crystallisation times found within the temperature range between 650 and 700 K (below $E < 10^8$ V/m) for the spherical particles (figure 5) has a much broader temperature range from approximately 600 to 800 K for the cylindrical particles (figure 6).

![Figure 6](image2.png)

**Figure 6.** Crystallisation times for cylindrical particle at different temperatures and electric fields.
4. Summary
We studied the electric field enhanced crystallisation kinetics in phase-change materials using nucleation theory. The crystallisation times are reduced for spherical shaped particles at larger electric fields, but on the other hand crystallisation of cylindrical shaped particles can be further enhanced at even lower fields.

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