Measurement of Onset of Structural Relaxation in Melt-Quenched Phase Change Materials

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Chalcogenide phase change materials enable non-volatile, low-latency storage-class memory. They are also being explored for new forms of computing such as neuromorphic and in-memory computing. A key challenge, however, is the temporal drift in the electrical resistance of the amorphous states that encode data. Drift, caused by the spontaneous structural relaxation of the newly recreated melt-quenched amorphous phase, has consistently been observed to have a logarithmic dependence in time. Here, it is shown that this observation is valid only in a certain observable timescale. Using threshold-switching voltage as the measured variable, based on temperature-dependent and short timescale electrical characterization, the onset of drift is experimentally measured. This additional feature of the structural relaxation dynamics serves as a new benchmark to appraise the different classical models to explain drift.

1. Introduction

When a liquid is quenched faster than its critical cooling rate, crystallization events can be overcome and atoms can structurally freeze into a disordered solid state.\(^1\) Upon cooling the melt, the atomic mobility decreases. Eventually, the system can no longer assume the equilibrium structure of the supercooled liquid state within the timescale of the experiment and a non-equilibrium glass state is created. The free energy difference between the super-cooled liquid and glass state results in structural relaxation, where the atomic configurations in the glass change over time. The intrinsic material properties, including viscosity, density, and the electronic bandgap, change due to relaxation.\(^3,4\) and this is understood to occur in three phases (Figure 1a).\(^6–8\) For every rearrangement, a finite energy barrier must be overcome, and therefore, for some amount of time, the onset phase, the properties do not change. In the second phase, where relaxation is most profound, the properties have been observed to change proportionally to \(\log(t)\). Finally, approaching the supercooled liquid, the glass reaches a saturation phase, and the properties no longer continue to change.

Tracking this structural relaxation process through all three phases is experimentally challenging. Most studies are focused on amorphous polymers and metallic glasses, yet there is little work on highly fragile glass formers with bad glass forming ability, such as phase change chalcogenide glasses.

Thin films of phase change chalcogenides, such as \(\text{Ge}_2\text{Sb}_2\text{Te}_5\) (GST) show interesting electrical and optical material properties, which can be rendered tunable via rapid and reversible crystalline to amorphous phase-transitions. Phase change chalcogenides are exploited for many technologies, including the commercialized electrical phase change memory (PCM) technology. In PCM, a nanoscale volume of a chalcogenide compound is sandwiched between the top and bottom electrodes. Joule heating, from current across the electrodes (Figure 1b), allows reversible amorphization and crystallization of the chalcogenide glass.\(^9\) The amorphous and crystalline states exhibit electrically distinct properties and thus, the device resistance can be toggled between a electrically conductive state (SET) and electrically distinct properties and thus, the device resistance can be toggled between an electrically conductive state (SET) and a resistive state (RESET). Within PCM devices, the amorphous state relaxes after RESET, and the observable metrics, such as the electrical resistance \((R)\) and the threshold-switching voltage \((V_{\text{th}})\), change due to structural relaxation. This process is commonly referred to as drift.\(^10\)

In the SET state, the device resistance increases with \(\log(R) = \log(R_0) + V_k \times \log(t/t_0)\), and the threshold-switching voltage increases with \(V_{\text{th}} = V_{\text{th},0} + V_{\text{th},0} \times \log(t/t_0)\), where \(V_k\) and \(V_{\text{th}}\) denotes the resistance and threshold voltage drift coefficients, respectively, \(R_0\) the resistance at \(t_0\) and \(V_{\text{th},0}\) the threshold voltage at \(t_0\). Importantly, however, these equations are only valid in the relaxation phase. What remains to be...
investigated both qualitatively and quantitatively are the other two phases, namely, when does structural relaxation begin and when does it end? To this end, measurements that capture the relaxation from extremely short to long timescales at different temperatures are required. Although drift in PCM devices has been studied extensively experiments only revealed the log \( t \) dependence of resistance and threshold voltage.\(^{[13,11,12]}\) A notable exception is a stand-alone sub-100 ns drift measurement by Ielmini et al. on GST that hints at the presence of a region where drift is absent.\(^{[3]}\) In Note S1, Supporting Information we compare these experiments to our study.

The goal of this study is to shed light on the phase where relaxation is absent. Specifically, to quantify on what timescales the commonly assumed log \( t \) dependence is valid, and to appraise the different classical models to explain drift. To this end, we employ \( V_{th} \) as a means to observe the state of relaxation. We study the drift characteristics of GST and a doped GST (dGST) by setting up a \( V_{th} \) drift measurement and analysis framework. Mushroom-type PCM devices of both materials are melt-quenched at temperatures spanning from 100 K to 300 K, and drift is probed from tens of nanoseconds to tens of seconds after RESET. The experimental data are fitted with two models, namely the collective relaxation and the Gibbs model of relaxation, and the different physical parameters used in the fitting are discussed and compared.

2. Threshold-Switching Voltage Drift Experiments

Because structural relaxation processes are thermally activated, ambient temperature can be used as a knob to shift the onset and saturation of drift to experimentally accessible timescales (see Figure 1a). However, the observation of the saturation phase by raising the ambient temperature (greater than 400 K) is prohibitive due to potential recrystallization of the amorphous phase. On the other hand, there is a potential for measuring the onset of drift by monitoring it at lower ambient temperatures. The challenge however, is the inability to reliably measure electrical resistance at short-timescales and low temperatures. Hence, we resort to \( V_{th} \) as a means to observe the state of relaxation. \( V_{th} \) marks the switching of the highly resistive RESET state to an electronically excited on-state (see Figure 2a).

To probe the \( V_{th} \) drift, the mushroom cell is repeatedly programmed to a new RESET state and SET pulses with delay times varying from 10 ns to 10 s are applied. Note that each \( V_{th} \) measurement results in the erasure by recrystallization of the corresponding RESET state. The measured \( V_{th} \) drift represents an averaged behavior of RESET states created in the device. Details on the experimental protocol and the algorithm to define \( V_{th} \) are provided in Section 6. Three distinct regimes are apparent in the temporal evolution (Figure 2b). In regime 1, up to \( \approx 1 \mu s \) there is a steep increase of \( V_{th} \). Most likely this is caused by the decay of the RESET excitation. While previous studies attributed this regime solely to decay of the electrical excitation,\(^{[11,14]}\) thermal transient effects may also play an important role. The threshold voltage increase with time in regime 1 appears to be independent of the ambient temperature (Note S2, Supporting Information). Regime 2 shows a flattening of the curve and almost constant threshold voltage values. Finally, in regime 3 we observe a continuous linear increase with log \( t \). We attribute the temporal evolution in regimes 2 and 3 to the structural relaxation of the amorphous phase with the transition between them marking the onset of relaxation.

In the following, we further analyze the temperature dependence of regimes 2 and 3 for GST and dGST. To create comparable RESET states at different ambient temperatures, the programming power was scaled such that the initially molten volume remains approximately constant (Note S3, Supporting Information) and the RESET pulse trailing edge was kept constant. Both materials show the same characteristic behavior (Figure 2c,d). With increasing ambient temperature, the \( V_{th} \) values decrease. This is due to the thermally activated transport of the amorphous phase. All experiments capture regime 2 in which \( V_{th} \) hardly changes. The transition point to regime 3, the onset of relaxation, shifts continuously to shorter timescales. Furthermore, the slope in regime 3 progressively increases with increasing temperature. Both these effects, namely, the onset shift and the slope change are expected because the relaxation processes are
accelerated by increasing temperature. At 100 K, we find \( V_{th} \) drift to be absent, which can be either because the drift coefficient is very small or because the onset has shifted outside of the measurement range. One possible reason for the former is that in a phase change material with trap states deep within the band gap, like Ge\(_2\)Sb\(_2\)Te\(_5\),[15–17] resistance drift at very low temperatures may not be observable if the electrical transport changes from a trap limited band transport to a hopping type transport. The activation energy for hopping would be defined by the distance between the Fermi level and the trap states, which may not necessarily change upon structural relaxation.

3. Analytical Framework and Relaxation Models

In this section, we will try to justify the use of \( V_{th} \) to monitor the state of relaxation and also to analyze the experimental data presented in Section 2 based on two different state-of-the-art relaxation models. We will start with some general considerations linking the evolution of an observable quantity (here \( V_{th} \)) with a variable \( \text{Glass}(t, T_{\text{hist}}) \) representing the state of relaxation, where \( T_{\text{hist}} \) captures the thermal history. \( \text{Glass}(t, T_{\text{hist}}) \) may be expressed differently depending on the relaxation model considered. (In the case of the collective relaxation model we will replace \( \text{Glass}(t, T_{\text{hist}}) \) with the abstract state variable \( \Sigma \), while in the case of the Gibbs model we will instead insert the number of defect states.)

Establishing an analytical relation between \( V_{th} \) and the state of relaxation poses a non-trivial problem. First, the exact mechanism of threshold switching is still debated, and second, it is not clear which material parameters change with relaxation. We assume that \( V_{th} \) can be defined by the sum of a temperature-dependent function \( f(T) \), a term proportional to \( \text{Glass}(t, T_{\text{hist}}) \) and an offset value \( C_2 \) that could change with the size of the amorphous dome for example.

\[
V_{th} = f(T) + C_1 \times \text{Glass}(t, T_{\text{hist}}) + C_2
\]  

A key basis for this assumption is the approximately linear change of \( V_{th} \) with the activation energy for electrical conduction (\( E_a \)).[18,19] \( E_a \) in turn has been shown to increase with drift.[12,20,21]
and a linear increase of $E_s$ with $\log(t)$ has been experimentally measured for different phase change materials.\cite{22,23} Thus, we expect that $V_{th}$ is proportional to $\text{Glass}(t, T_{\text{init}})$. Finally, we assume that the change of $V_{th}$ upon relaxation is decoupled from the change of ambient temperature $T$. Such a decoupling was previously deduced in\cite{24} and can also be derived from simulations based on a thermally assisted switching model (see Note S4, Supporting Information).\cite{19}

From Equation (1), it can be seen that the temporal change in $V_{th}$ with respect to a defined reference point, $t_{\text{ref}}$, is dependent only on $\text{Glass}(t, T_{\text{init}})$. For our analysis, we identify $V_{th}$ (1 $\mu$s) as an ideal reference point where drift is absent for all temperatures studied. We denote the initially created glass state, that did not yet begin to relax, as $\text{Glass}_0$.

$$\Delta V_{th} = V_{th}(t, T) - V_{th}(1 \mu s, T) = C_1 \times (\text{Glass}(t, T_{\text{init}}) - \text{Glass}_0) \tag{2}$$

In the following, we will show that, based on these assumptions, the temperature-dependent onset of threshold voltage drift can be captured with two common relaxation models proposed for phase change materials, that is the Gibbs model\cite{25,26} and the collective relaxation model.\cite{12,27}

### 3.1. Collective Relaxation Model

The collective relaxation model does not specify individual relaxation processes or defect states but instead quantifies the relaxation state of the glass by an abstract state variable $\Sigma$. $\Sigma = 1$ is an infinitely unrelaxed state and $\Sigma = 0$ denotes that the system approaches equilibrium.\cite{28} Upon relaxation, the system assumes configurational states of progressively lower energy. The activation energy $E_0 = E_s \times (1 - \Sigma)$ that must be overcome for the next relaxation step increases monotonically. The temporal evolution of the state variable $\Sigma$ is captured by the rate equation

$$\frac{d\Sigma(t)}{dt} = -v_b \Delta\Sigma \times \exp \left( \frac{-E_s \times (1 - \Sigma(t))}{k_b T} \right)$$

assuming an Arrhenius dependence of the relaxation rate on the activation energy. The attempt to relax frequency, which is on the order of phonon frequencies, is denoted by $v_b$ and $\Delta\Sigma$ is the change of $\Sigma$ with each relaxation step. Consequently, $\Delta\Sigma \times E_s$ defines the increase of the activation energy for each subsequent relaxation step. For a constant ambient temperature, the differential equation can be solved analytically as

$$\Sigma(t, T) = -\frac{k_b T}{E_s} \log \left( 1 + \frac{\tau_0}{\tau_1} \right)$$

with $\tau_0 = \frac{k_b T}{v_b \Delta\Sigma E_s} \exp \left( \frac{E_s \times (1 - \Sigma_0)}{k_b T} \right)$ marking the begin of relaxation from the initial glass state $\Sigma_0$ and $\tau_1 = -\frac{k_b T}{v_b \Delta\Sigma E_s} \exp \left( \frac{E_s}{k_b T} \right)$ the time at which the system reaches equilibrium. In the range $\tau_0 < t < \tau_1$ the temporal evolution of $\Sigma$ follows $\log(t)$ and the change of $\Sigma$ depends linearly on the ambient temperature. The linear temperature dependence of $\tau_0$ is almost negligible compared to the exponential term. In a first approximation the shift of the relaxation onset with temperature is defined by the smallest activation energy for relaxation $E_{\text{min}} = E_s \times (1 - \Sigma_0)$ and the effective attempt to relax frequency $v_b \Delta\Sigma$ is a scaling factor defining the timescale of the onset.

To fit the experimental data with the collective relaxation model, the terms $\text{Glass}(t, T_{\text{init}})$ and $\text{Glass}_0$ in Equation (2) are replaced by $\Sigma(t, T)$ and $\Sigma_0$ respectively. Both distinct features, the shift of the onset $\tau_0$ and the increase of the drift coefficient $V_{th} = C_1 \times k_b T/E_s$ with ambient temperature are well captured (Figure 3). It confirms that the observed threshold.

### Table 1. Fitting parameters—collective relaxation model.

| Material | $C_1/E_s$ [V/eV] | $v_b \Delta\Sigma E_s$ [eV s$^{-1}$] | $(1 - \Sigma_0)E_s$ [eV] |
|----------|-----------------|---------------------------------|-----------------|
| GST      | $-1.2$          | $2.48 \times 10^6$              | $0.19$           |
| dGST     | $-0.73$         | $1.07 \times 10^8$              | $0.24$           |
voltage evolution is caused by the relaxation dynamics of the amorphous phase. At 300 K, \( \tau_0 \) of GST and dGST is \( \approx 15 \) μs and \( \approx 2.3 \) μs after RESET, respectively. Interestingly, the relaxation onset of the glass states created at ambient temperatures ranging from 100 K to 300 K can be fitted with a single \( \Sigma_0 \), that is, the degree of relaxation of the initially created glass state does not change notably. Faster quenching has been observed to create less relaxed glass states.[29] In our study the cooling profile of the melt-quenching process changes with ambient temperature. An understanding of the quench-rates and glass transition temperature in the device and how these determine the initial value of \( \Sigma_0 \) could be subject of future work.

Still it is not possible to determine unique values of \( \Sigma_0, C_i, E_d \) or \( v_0\Delta \xi_q \), the material parameters defining the relaxation kinetics. To this end it would be necessary to also determine the time of drift saturation \( \tau_s \). As long as only the drift coefficient \( v_{0\Delta \xi} \) and \( \tau_s \) are known, the four fitting variables are interdependent. The drift coefficient depends on \( C_i/E_d \) the exponential prefactor of \( \tau_s \) on \( v_0\Delta \xi E_d \) and the exponential term on \( (1 - \Sigma_0/E_d) \).

The variable \( E_d \), which defines the activation energy for relaxation as the glass approaches its ideal state, is constrained to some extent. Defining the longest times for which drift is reported in the literature as a lower limit for \( \tau_s \), we calculate a lower limit for \( E_d \). In pure GST, drift was measured for more than \( 8 \times 10^7 \) s at 300 K[31] and in a dGST, similar to the one used in this study, drift for \( 10^8 \) s at 420 K[32] has been reported. This corresponds to a lower limit of 0.95 eV and 1.12 eV for GST and dGST, respectively. The upper limit of \( E_d \) is on the order of the activation energy of crystallization, which is 3.2 eV for GST[30] and 3.01 eV for dGST.[31]

At this point, it is worth highlighting the simplicity of this model, which has been shown to not only capture relaxation at a constant ambient temperature but also the effect of annealing profiles on the resistance in phase change memory devices.[27] Only two variables, \( v_0\Delta \xi \), and \( E_d \) define the relaxation dynamics and, since relaxation is abstracted to a collective process, a single variable suffices to describe the degree of relaxation of the glass state.

### 3.2. Gibbs Model

The relaxation model introduced by Gibbs in the 1980s defines the glass by a spectrum of defect states with different activation energies \( (q(E_d)) \).[32] The sum of these defect states \( (Q) \) and their change with time is the equivalent of \( \Sigma(t) \) in the collective relaxation model. While the physical picture of the relaxation process is different, the models are mathematically quite similar. Like in the collective relaxation model, a rate equation with an Arrhenius dependence on the defect state activation energy for relaxation \( (E_d) \) is assumed

\[
\frac{dq(E_d,t)}{dt} = -v_0 \times \exp \left( -\frac{E_d}{k_B T} \right) \times q(E_d,t)
\]

where \( v_0 \) is the attempt to relax frequency. Since the probability to relax depends exponentially on the activation energy for relaxation, defects with a small activation energy relax first and only defects in a narrow range of activation energies relax at the same time (see Note S5, Supporting Information). Thus, the activation energy that must be overcome for further relaxation effectively increases monotonically, like in the collective relaxation model. For a constant ambient temperature, the relaxation dynamics are given by the equation

\[
Q(t,T) = \int q(E_d) \times \exp \left(-\tau \times v_0 \times \exp \left(-\frac{E_d}{k_B T} \right) \right) dE_d
\]

Accordingly, the terms Glass\((t,T_{\text{hist}})\) and Glass\(_0\) in Equation (2) are replaced by \( Q(t,T) \) and \( Q_0 \), the initial number of defect states, respectively to fit the experiments.

The main challenge in probing the Gibbs model is to infer what spectrum of defect states the material has. Experimental studies on other materials show bell-shaped or more complex distribution functions.[13–17] To capture the strict \( \log(t) \) dependence observed in phase change materials over many orders of magnitude in time, a rather flat \( q(E_d) \) is required.[12,13,28] The onset of relaxation emerges from a transition from no defects to existing defects. How sharp it depends on the width of this transition and the attempt to relax frequency. We fit the experiment assuming three different initial defect distributions \( q_0(E_d) \).

One with a step-like transition and two with a linear transition over an energy range of 0.25 eV and 0.5 eV (Figure 4). The upper limit of \( q_0(E_d) \) is set to 1.5 eV, which is well beyond the highest activation energies that can be overcome on the timescales and temperatures probed in our study. The position of the transition, the attempt to relax frequency and the proportionality constant \( C_i \) are free fitting parameters. All three distributions give a fairly good fit to the experimental data. An extrapolation to longer timescales, however, shows that the onset is stretched out too much for the 0.5 eV wide transition. In both materials, the \( q(E_d) \) needs to have a rather sharp transition from zero to a constant number of defects.

### 4. Discussion

The onset of relaxation constrains the parameters in both relaxation models. The activation energy that must be overcome for the first relaxation step in the collective relaxation model is 0.19 eV for GST and 0.24 eV for dGST. In the Gibbs model, the equivalent to this is the position of the transition from no defects to existing defects, which is at around 0.1 eV to 0.25 eV for both materials (Figure 4, inset). It changes slightly depending on the assumed shape of \( q(E_d) \). In the phase change memory cell, a melt-quenched state is created with extremely high cooling rates on the order of \( 10^{10} \) K s\(^{-1}\). It thus allows studying the relaxation from an extremely unrelaxed glass state, which manifests in the low activation energy for relaxation and consequently an onset of relaxation at short time scales.

Another parameter used in both models is the attempt to relax frequency \( v_0 \) (Equations (3) and (5)). Previous studies on phase change materials estimated the attempt to relax frequency in the typical phonon frequency range of \( 10^{13} \) to \( 10^{14} \) s\(^{-1}\).[12,25] Our fits to the Gibbs model give an attempt to relax frequency on the order of \( 10^7 \) s\(^{-1}\) to \( 10^8 \) s\(^{-1}\) for GST and \( 10^8 \) s\(^{-1}\) for dGST, which is notably lower than previously considered for phase change materials. In order to fit experimentally obtained relaxation
have been found.\[38\] To fit the relaxation of nanoscale indents has been used.\[39\] We believe that to justify the Gibbs model, in the collective relaxation model is of magnitude, is required. The corresponding fitting parameter attempt to relax frequency could change over so many orders further explanation, and physical reasoning, as to why the attempt to relax frequencies ranging from $10^{11}$ to $10^{15}$ s$^{-1}$ have been reported. Here, reduced attempt to relax frequencies were ascribed to relaxation processes involving groups of atoms.\[37\] In carbon doped amorphous silicon frequencies as low as $10^{10}$ s$^{-1}$ have been found.\[38\] To fit the relaxation of nanoscale indents in a polymer glass an attempt to relax frequency of $2 \times 10^{14}$ s$^{-1}$ has been used.\[39\] We believe that to justify the Gibbs model, further explanation, and physical reasoning, as to why the attempt to relax frequency could change over so many orders of magnitude, is required. The corresponding fitting parameter in the collective relaxation model is $v_0 \Delta_x$ which is $\approx 10^8$ s$^{-1}$ for GST and $\approx 10^9$ s$^{-1}$ for dGST. The variable $\Delta_x$ is expected to be $\ll 1$; $1/\Delta_x$ is the hypothetical number of the different configurational states that the system could assume. Accordingly, the collective relaxation model requires orders of magnitude higher attempt to relax frequencies than the Gibbs model. In this case we can expect attempt to relax frequencies of $10^{13}$ to $10^{14}$ s$^{-1}$.

A major critique against the Gibbs model concerns the shape of the activation energy spectrum required to capture the drift of phase change materials. Studies on metallic glasses found bell shape or more complex spectra with a rather shallow increase of the number of defect states over a range of 0.5 to 1 eV.$^{[34–37]}$ Opposed to this, to explain the $\log(t)$ dependent drift observed over many orders of magnitude in time a rather flat spectrum of defect states over a range of at least 1 eV is required.$^{[32]}$ Additionally, to capture the relaxation onset, the transition between no defects to existing defects must happen in a narrow energy range. The threshold voltage drift characterized here represents an average behavior of multiple RESET states created in the device. Thus, the relaxation onset is blurred, and the characterization of a single glass state would probably show an even sharper relaxation onset. A sharp onset also requires a sharp transition of $q(E)$. These considerations indicate that an almost step-like $q(E)$ is required to capture the relaxation onset in phase change materials. This provides further evidence that an improbable $q(E)$ is required to explain the drift of phase change materials with the Gibbs model. In fact, for the scenario of a step-like transition, the Gibbs model and the collective relaxation model give identical fits to our experimental data (Note S5, Supporting Information). To constrain $q(E)$ further, relaxation studies over even longer timescales are required.

Two recently proposed relaxation models postulate that resistance drift may also result from the release of trapped electrons. The release of these charge carriers has been proposed to increase the width of the potential barrier needed to overcome at the contact between electrode and phase change material.$^{[40]}$ A second hypothesis states that these electrons recombine with thermally generated holes in the valence band and thus reduce the number of free charge carriers in the amorphous state.$^{[14]}$ Even though these models assume quite a different mechanism, they could in principle explain the onset and saturation of drift. The onset of drift would be determined by the potential barrier and attempt to escape frequency of electrons from a trap state. Drift would saturate when an equilibrium between electron trapping and detrapping is reached. In the current version, however, the model proposed in$^{[14]}$ is designed such that drift begins immediately after RESET. Neither of the two

Table 2. Fitting parameters—Gibbs model: The threshold voltage drift is fitted with three differently shaped initial activation energy spectra $q_0(E_d)$ (inset, Figure 4); dependent on the spectrum the attempt to relax frequency and the proportionality constant between $V_{th}$ and the sum of defect states changes.

| Material | Transition $q(E)$ | $v_0 [s^{-1}]$ | $C [\text{V}]$ |
|----------|-------------------|--------------|---------|
| GST      | step              | $3.66 \times 10^{-7}$ | −1.57 |
| GST      | 0.25 eV           | $7.33 \times 10^{-8}$ | −1.54 |
| GST      | 0.5 eV            | $8.64 \times 10^{-7}$ | −2.33 |
| dGST     | step              | $2.27 \times 10^{-9}$ | −0.92 |
| dGST     | 0.25 eV           | $1.97 \times 10^{-9}$ | −1.00 |
| dGST     | 0.5 eV            | $9.33 \times 10^{-9}$ | −1.15 |

Figure 4. Model fit - Gibbs model: The temporal evolution of the threshold voltage of GST (a) and dGST (b) is fitted to the Gibbs model for three differently shaped activation energy spectra. The initial defect distribution functions $q_0(E_d)$ are shown in the figure inset. When the activation energy spectrum increases over an energy range that is too wide, here $0.5 \text{ eV}$, the onset gets stretched out too much. For better visibility the experiments at different temperatures are shifted along the y-axis by $\left( T_{\text{amb}} - 100 \text{ K} \right) \times 0.2 \text{ V/K}$. The fitting parameters are summarized in Table 2.
models specifies the expected dynamics of electron detrapping. Thus, we cannot say if or how well these models will be capable of quantitatively capturing the temperature-dependent onset of relaxation.

In this work we capture the onset of relaxation with two phenomenological models for structural relaxation. Ab initio molecular dynamics and classical molecular dynamics simulations, with machine-learning interatomic potentials, offer an alternative approach to study drift and relaxation of phase change materials. Here, knowledge of the onset of relaxation could lead to new insights about the structural arrangement of the melt-quenched device state.

5. Conclusion

In this work we experimentally measured the onset of structural relaxation in melt-quenched amorphous phase-change materials. Threshold-switching voltage was used to measure the state of relaxation. Experiments were performed using mushroom-type phase-change memory devices with GST and doped GST as phase-change materials. The onset of structural relaxation, marked by a transition from almost constant threshold-switching voltage values to the commonly observed log(t) dependence, changes profoundly with ambient temperature; from microseconds at 300 K to tens of seconds at 100 K. We found that both the Gibbs relaxation model and the collective relaxation model are capable of describing the experimental data. The fits to the Gibbs model, however, required an almost step-like defect distribution and orders of magnitude lower attempt to relax frequencies than estimated in previous works.

6. Experimental Section

**Mushroom-Type PCM Device:** The mushroom-type PCM cells used in this study were fabricated in the 90-nm technology node. The multi-layer ring bottom electrode with a radius of ~20 nm and a height of ~40 nm was patterned with a sub-lithographic hardmask process. The sputter deposited phase change material is ~75 nm thick. To assure a stable device operation throughout our study the cells were cycled at least 100000 times in advance. The devices are fabricated with an on-chip series resistor of ~2 kΩ.

**Experimental Setup:** The experiments were performed in a cryogenic probe station (JANIS ST-500-2-UHT), cooled with liquid nitrogen, that operates between 77 and 400 K. The sample holder and chamber temperature was controlled with an accuracy of ±0.5 K. AC voltage signals were applied to the device with an Agilent 81150A Pulse Function Arbitrary Generator. To send the SET pulse (Instrument Output 1) with a defined delay time after the RESET pulse (Instrument Output 2), the two instrument outputs were coupled internally. Cell voltage and current were measured with a Tektronix DPO5104B digital oscilloscope, which was triggered on the SET pulse leading edge. The transient signals were sampled with a frequency of 2.5 GHz.

**Experimental Protocol:** In order to measure the threshold voltage evolution with time the device is programmed to a new RESET state multiple times and the pause tplay before applying the SET pulse is increased. This sequence with a tplay ranging from 10 ns to 10 s is repeated 15 times to average out drift and threshold switching variability. Due to the variability some scattering of the data and potentially a blurring of the onset of relaxation is inevitable. Nonetheless the overall threshold voltage change with time is a smooth curve. The standard deviation is around 30 mV for GST and 50 mV for dGST.

**Definition of the Threshold Voltage:** To extract the threshold voltage from the switching IV curve we fit the load-line of the voltage snap-back (Note S5, Supporting Information). The mushroom cell is fabricated with an on-chip series resistor. In the moment of switching the cell resistance drops to values similar to the series resistor (Rseries) and thus the voltage drop over the cell decreases. By fitting the load-line, instead of choosing the largest voltage drop prior to switching as threshold voltage value, the analysis scheme becomes more resilient to noise in the transient voltage and current trace. The threshold voltage is defined at a load-line current of 5 μA.

**Impact of the SET Pulse Shape on Vth:** To induce threshold switching the device is biased with a triangular voltage pulse. Both, the electrical stress and joule heating in the device prior to switching, may affect the relaxation dynamics of the device. In fact, the threshold voltage of a nanoscale device changes dependent on the transient voltage signal applied in order to switch the device. With an increasing duration of the SET pulse leading edge, the threshold voltage decreases (Figure S5a, Supporting Information). The absolute change of Vth with time, however, appears to be independent of the leading edge (Figure S5b, Supporting Information). This suggests that the rise of the cell bias is fast enough to not notably alter the relaxation process of the glass state prior to switching. First, the time for which the cell is biased prior to switching is short on absolute time scales. Second, it is at least in regime 2 and 3, which are governed by the relaxation dynamics, much shorter than the time for which the material relaxes without any bias being applied.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Data available on request from the authors.

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