Measurement of Crystal Growth Velocity in Melt-Quenched AgInSbTe – Viscosity and Glass Formation in Phase Change Materials

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ABSTRACT

The temperature dependence of the crystal growth velocity of the phase change material AgInSbTe is derived from laser-based time-resolved reflectivity measurements. We observe a strict Arrhenius behaviour for over eight orders of magnitude (from ~10nm/s to ~1m/s). This can be attributed to the formation of a glass by quenching of the melt. From these data the temperature dependence of the viscosity is derived, which reveals that the supercooled liquid phase must have an extremely high fragility (>100). This value is extraordinarily large for an inorganic material. The new experimental evidence leads to an interpretation, which explains existing data from other crystal growth experiments, calorimetric measurements and even stress relaxation experiments on the same material in a comprehensive way. This is accomplished by embracing the structural dynamics of a glass, in particular structural relaxation and the cooling-rate dependence of the glass transition. The resulting insight has direct relevance for both switching speed and data retention in phase change memories.

Key words: crystallization kinetics, growth velocity, laser reflectivity, viscosity, glass transition, melt-quenching, fragility, data retention, switching speeds, structural relaxation

1. INTRODUCTION

So far measurements of crystal growth velocity have been limited to rather low temperatures where crystallization speeds are still slow⁷−¹⁰. It was only very recently that Orava et al. undertook a vast extension of the range of investigated crystallization speeds using ultra-fast differential scanning calorimetry and derived information on the crystal growth velocity. In this study the as-deposited amorphous phase was investigated under non-isothermal conditions¹¹. In the past, fast measurements have always been performed in a non-isothermal way employing short laser or voltage pulses to crystallize a small volume of material causing severe difficulties to obtain the temperature dependence of nucleation and growth velocities¹²−¹⁵.

In this work (originally published in Nature Communications, August 2013), we take a new approach to quantify the temperature dependence of the crystal growth velocity $u(T)$. Our laser-based method allows the investigation of the technologically relevant melt-quenched amorphous phase under isothermal conditions. At the same time, the new technique is capable of providing experimental data over a large range of crystal growth velocities (8 orders of magnitude) reaching up to the fastest regime (>1m/s). This unprecedented quantitative experimental evidence will lead to far-reaching conclusions about the viscosity of the material under investigation, here AgInSbTe, not only in the melt-quenched amorphous solid but also in its supercooled liquid phase.

2. EXPERIMENTS

Laser reflectivity measurements. To determine the crystal growth velocity in a thin film of phase change material, time resolved reflectivity measurements with a bi-chromatic laser setup were
An intense laser pulse is used to locally melt a cylindrical volume with a radius of several hundred nm in a thin crystalline phase change film. In this study AgInSbTe is chosen as material under investigation, because it is successfully applied in data storage technologies and many relevant physical properties have been experimentally quantified for this alloy in the past. This material is sandwiched between two layers of transparent ZnS-SiO₂ as depicted in the insets of fig. 1. Once the laser pulse ends, the heat is very efficiently dissipated out of the melt into the Silicon substrate creating a melt-quenched mark. Finite element simulations of the layer stack show that it takes no longer than 100 ns to cool the phase change material down to the temperature of the substrate (blue curve in fig. 1). A second, low-intensity continuous-wave laser probes the reflectivity of the layer stack at exactly the same position where the first laser melts the phase change material (black curve in fig.1). The reduction of reflectivity is a measure for how much of the previously crystalline material is amorphized. After thermalization, the gradual recovery back to a high reflectivity is thus an indicator for the progress of recrystallization. During the whole experiment, the sample is heated homogeneously at the temperature for which crystallization will be studied. The laser heating, however, is only used for the initialization of a crystallization experiment by creating an amorphous mark. This is crucial to obtain quantitative results for the temperature dependence of the crystal growth velocity using minimal assumptions. Since the sample first needs to return to the substrate temperature, there exists an upper limit for the measurable crystallization speed. For AgInSbTe this limit is reached at a temperature of ~550 K. To obtain meaningful data the crystallization time must be significantly longer than the quenching time, i.e. longer than 100 ns. This time corresponds to a crystal growth velocity of some m/s. While the collected data reach down to around 10 nm/s, the present method can be even used for slower crystal growth velocities at the expense of longer measurement times. Hence we can follow crystal growth over a wide range of temperatures.

**Figure 1 (left): Time resolved reflectivity measurement and simulated temperature profile.** The black line is the reflectivity trace collected during a recrystallization experiment performed at a substrate temperature of 533K. The zero of the timescale corresponds to the creation of the amorphous mark by the application of a laser pulse (83 mW for 30 ns at 658 nm wavelength). At this time the reflectivity suddenly decreases (red ellipse) and then, due to the recrystallization process (green ellipse), it increases again up to a steady state value (yellow ellipse) that corresponds to the complete recrystallization. The blue line shows the temperature profile during the laser irradiation process, simulated employing a finite element method.

**Figure 2 (right): Recrystallization experiments probed by Transmission Electron Microscopy (TEM).** The phase transition occurs via crystal growth from the amorphous-crystal interface. The TEM image of section (e) refers to the annealing of an AgInSbTe sample at 473K. No structural contrast between the recrystallized bit and the crystalline matrix is visible. When the same experiment (493K) is performed using Ge₂Sb₂Te₅ the recrystallization is nucleation-dominated and the erased bit has a pronounced contrast in comparison to the crystalline matrix (f). More detailed information about the different figures (a)-(f) are given in the original publication of this work in Nature Communications, August 2013.

**Confirmation of growth dominated crystallization via TEM.** The second major source of complication in interpreting experimental data on crystallization kinetics, besides the lack of
isothermal conditions, is the entanglement of nucleation and growth. This problem is overcome here as the recrystallization of the amorphized mark takes place solely by growth of the crystal-to-amorphous interface from the rim to the centre. This has been verified by transmission electron microscopy (TEM). The top row of figure 2 reports a series of micrographs showing that recrystallization of a mark annealed in-situ at ~383 K occurs exclusively by crystal growth from the rim. This kind of in-situ analysis can obviously only be performed in the slow crystallization regime. To obtain experimental evidence for the growth domination also in the ultra-fast regime, i.e. at higher temperatures, ex-situ TEM measurements were performed. An amorphized mark that is erased by growth of the surrounding crystallites should be indistinguishable from its crystalline environment. Figure 2(c) shows a TEM micrograph of an amorphous mark recrystallized at 473 K, a temperature in the middle of the investigated range. The contrast that is visible in this TEM image is solely due to a bending of the lattice inside large crystallites\(^{18, 19}\). No structural difference is visible between the recrystallized bit and its environment. This feature, observed also in fig.2(c), verifies that a growth-dominated process is also active in the fast regime at elevated temperatures. A very different TEM micrograph is expected if nucleation also plays a considerable role in the crystallization process. This is confirmed by a comparable experiment performed for Ge\(_2\)Sb\(_2\)Te\(_5\). Here, nucleation interferes in the recrystallization process and the size of clearly distinguishable crystallites inside the bit is even smaller than in the surrounding poly-crystalline phase (see fig. 2f).

**Determination of crystal growth velocity.** The erasure of the amorphous bit in the film of phase change material takes place by growth from the rim as verified in the above section. Thus the crystal growth velocity at a given temperature can be calculated by dividing the radius \(r\) of the created mark at the beginning of the recrystallization process by the time it takes for the reflectivity to fully recover. The initial radius \(r\) is computed from the drop in reflectivity induced by the laser pulse while taking into account the intensity profile of the probe laser and the dielectric function of all materials in the layer stack. This method was cross-checked by comparing the radius resulting from this calculation with both ex-situ transmission electron microscopy (TEM) analyses and finite elements calculations of the laser-induced melting of the film (for more details see Methods section and Supplementary Note 4 of the original publication of this work in Nature Communications, August 2013). A good quantitative agreement was found between the different techniques. In the light of the above explanations it is apparent how the design of our experiment enables a data analysis making as few assumptions as possible. Experimental evidence has been presented which justifies each step of the analysis\(^{17, 22}\).

3. RESULTS & DISCUSSION

**Crystal growth velocity.** For AgInSbTe our laser experiments result in the crystal growth velocity as a function of temperature between 418 K and 553 K as plotted in figure 3. The measured recrystallization times range from several seconds down to some hundred nanoseconds, and correspond to crystal growth velocities spanning eight orders of magnitude from around 100 nm/s at 418 K up to more than 3 m/s at 553 K. The experimental data fit nicely to an Arrhenius law (with activation energy of 2.7eV), as one would expect for a glass. In the same figure, the data available in literature for AgInSbTe\(^7\) are displayed. It is noteworthy that those measurements are performed in the as-deposited amorphous phase. Those data are not only restricted to the slow end of the growth velocity scale, but they also extend over a much narrower range of temperature. The comparison with our data on melt-quenched samples shows that as-deposited films exhibit a much slower growth velocity at a given temperature. This demonstrates how crucial it is to measure \(u(T)\) for the technologically relevant melt-quenched state to derive realistic estimates of device performance. Indeed, different retention times and switching speeds for amorphous as-deposited and melt-quenched devices have already been reported for different phase change materials, e.g. Ge\(_2\)Sb\(_2\)Te\(_5\) and doped SbTe\(^{23, 25}\). The data presented in figure 3 now provide an explanation for these observations.

Although the data in figure 3 end at 553 K for experimental reasons, it can be clearly seen that it is not possible to extend the Arrhenius behaviour of \(u(T)\) up to the melting point (\(T_m=808\)K). Assuming this trend, the speed of sound in amorphous AgInSbTe (~1000 m/s) would be overcome at around 625 K.
Furthermore, using a two-pulses experiment the maximum crystal growth velocity can be estimated to be between 10 m/s and 100 m/s (for details see Supplementary Note 1 of the original publication of this work in Nature Communications, August 2013). As previously stated, at 553 K a value of 3.4 m/s is measured, not very far from this maximum. Hence, at higher temperatures, a quite dramatic change in the temperature dependence of the crystal growth velocity must occur. It is reasonable to suspect that the origin of this change is related to the intrinsic characteristics of the disordered phase.

**Figure 3 (left): Temperature dependence of crystal growth rate.** The growth velocity in melt-quenched amorphous AgInSbTe (red circles) as measured by the optical tester. The red pentagon refers to the in-situ TEM recrystallization experiment reported in figure 2. A similar behaviour has been measured over a much smaller range of velocities and temperatures in as-deposited blanket AgInSbTe thin films (blue squares).

**Figure 4 (right): Temperature dependence of viscosity.** Reversing equation (1) and using the growth velocity measurements of figure 3 we have calculated the viscosity of AgInSbTe as a function of temperature (filled red circles). The general understanding that a glass is formed upon cooling from a supercooled liquid implies that the curves of supercooled liquid (continuous lines) and glass (red triangles) have to connect. The lines (black and red) are obtained by fitting the equation proposed by Mauro et al. for the description of the viscosity of a supercooled liquid to the laser results at the 11 highest measured temperatures together with literature values for the viscosity in the liquid phase (in case of the black line the experimentally determined viscosities in liquid Sb80Te20, an alloy close to the base stoichiometry of the AgIn-doped SbTe used in the present work, from Ref. 26 represented by the open black circles; and in case of the red line the theoretically derived viscosity of AgInSbTe from Ref. 27 represented by the red open circle). Both fits correspond well with a viscosity of 10^{12} Pas at the glass transition temperature Tg=443K (green filled circle) that was previously observed for AgInSbTe using calorimetry. The blue squares are obtained using the data on as-deposited AgInSbTe reported in ref. 7. The original viscosity values derived from growth velocities (red filled circles from current laser experiments and blue filled squares from previous studies on as-deposited amorphous AgInSbTe) are corrected for structural relaxation they had time for during the experiments resulting in open red and open blue triangles, respectively. (More detailed information about this correction is given in the original publication of this work in Nature Communications, August 2013)

**Transfer to viscosity.** In order to develop a comprehensive interpretation of the various observations on crystallization kinetics in phase change materials, we need to discuss the glass dynamics of these alloys. Therefore, we derive values for the viscosity η of AgInSbTe from the measured crystal growth velocities u employing the fact that the temperature dependence of u is tightly connected with the temperature dependence of η. To calculate the viscosity, the reversed form of the following equation is used:

\[
  u(T) = \frac{4\pi r_{\text{atom}}^2 k_B T}{3\pi \lambda^2 R_{\text{HDA}} \eta(T)} \left( 1 - \exp \left( -\frac{\Delta G(T)}{k_B T} \right) \right) \tag{1}
\]
Here $r_{\text{atom}}$ is the atomic radius (the half of the bond length, 1.5 Å), $\lambda$ is the diffusional jump distance (~1 Å), $\eta(T)$ is the viscosity of the disordered surrounding, $k_B$ is the Boltzmann constant, $\Delta G(T)$ is the Gibbs energy difference between the liquid and the crystalline phase, $R_{\text{hyd}}$ is the hydrodynamic radius (~0.5 Å). The latter has been estimated by the Stokes-Einstein equation, applied at the melting point, using the data of viscosity and atomic diffusivity reported in $^26$ $^27$. The Gibbs energy gain has been estimated using the Thompson-Spaepen approximation$^28$, for which the heat of fusion $\Delta H_{\text{fus}}$ (173 +/- 3.1 meV/atom) and the melting temperature $T_m$(808 K) have been extracted from ref. $^29$. In the temperature range probed, the change of the exponential term in equation (1) is so small (i.e. $0.9<\Delta G(T)/k_B T<1.6$) that it cannot account for more than a change of 26% in $u(T)$. This clearly shows that the change of $u(T)$ over eight orders of magnitude is dominated by the temperature dependence of $\eta(T)$. Hence, the viscosity also exhibits an Arrhenius dependence on temperature, as can be seen in figure 4. As for $u(T)$, also for $\eta(T)$ the experimentally determined Arrhenius behaviour cannot extend to much higher temperatures, since the viscosity value at around 550 K (~170 mPas) is not even two orders of magnitude away from the viscosity measured in the liquid (~2 mPas)$^26$. Such a pronounced flattening out of $\eta(T)$ (and thereby also of $u(T)$) towards higher temperatures can only be realized if a material’s supercooled liquid phase has a high fragility. The strong bending of the $\eta(T)$-curve that comes with a high fragility is, however, incompatible with the straightness of the experimental data at lower temperatures. Our experimental data cannot be described by the theoretical formulas for a supercooled liquid phase (not even if a breakdown of Stokes-Einstein-relation is allowed). We consequently interpret our data as representing a melt-quenched glass for which the atomic configuration deviates from the equilibrium configuration of the supercooled liquid at a rather high temperature due to the vast cooling rates employed.

Because glasses are non-equilibrium solid states, we next consider the implications of structural relaxation for experimental determinations of crystallization rates. (More details about this can be found in the more extensive original publication of this work in Nature Communications, August 2013). The corrected viscosities are added into fig. 4 both for melt-quenched (red triangles) and as-deposited amorphous (blue triangles). The reason for the corrections being very small for the melt-quenched state lies in the concept of the new laser method, i.e. in measuring recrystallization purely by growth from a pre-existing crystalline interface, so there is no waiting time between preparation of the amorphous state and the actual measurement.

**Viscosity of the supercooled liquid.** As can be nicely seen in fig. 4, in order to bring the viscosity of the supercooled liquid phase of AgInSbTe up from the viscosity of the liquid phase$^26$ (around 10$^3$ Pas) in a way that it is in line with the values derived from our measurements, extremely high fragilities are necessary. (The kinetic fragility $m$ is defined as the steepness of $\eta(T)$ at the glass transition temperature $T_g$, i.e. $m=\left(d \log_{10} \eta(T) / d T\right)_{T=T_g}$) The general understanding that a glass is formed upon cooling from a supercooled liquid implies that the curves of supercooled liquid (continuous lines) and glass (red triangles) have to connect. Using the equation proposed by Mauro et al.$^38$ for the description of the viscosity of a supercooled liquid, the fragility turns out to be $m=135$ ($T_g=445$K, $\eta_g=1.22 \times 10^3$ Pas) fitting the laser results at the highest temperatures together with the experimentally determined viscosities in liquid Sb$_{80}$Te$_{20}$ from Ref. $^26$ (open black circles). Fitting the same laser results together with a value $\eta(T=850K)=1.1 \times 10^3$ Pas for the viscosity of liquid AgInSbTe as derived in theoretical simulations (open red circle, data taken from supplementary information for Ref. $^27$) still results in a fragility of $m=128$ ($T_g=443$K, $\eta_g=0.58 \times 10^3$ Pas). Both fits correspond well with a viscosity of 10$^{12}$ Pas at the glass transition temperature $T_g=443$K that was previously determined for AgInSbTe using calorimetry$^39$.

While our experimental data necessitate the supercooled liquid to be highly fragile, the theoretical formulas for supercooled liquids fail to describe the whole set of experimental data (even when decoupling of diffusivity and viscosity is considered). Therefore, unlike the supercooled liquid curve, the blue and red triangle symbols in fig. 4 represent two fixed (but mutually different) configurations of the glass (iso-configurational line). In this light, the difference between viscosities (and crystal growth velocities) in the melt-quenched and the as-deposited state can be attributed simply to a
different configuration or degree of relaxation. In that sense an amorphous state that is produced by quenching from the melt in less than 100 ns can be expected to be a highly unrelaxed glass; apparently less relaxed than an amorphous sample that was produced by sputter deposition and crystallized at a considerably later time. In this way, the faster crystallization in the melt-quenched amorphous state can be understood.

4. CONCLUSION

The outcome of a very high fragility for AgInSbTe resulting from the above interpretation is in line with a generally observed correlation between a high fragility and a large difference in configurational entropy or heat capacity between the liquid and amorphous phase of a material. It is remarkable though, that other materials with high fragility, i.e. typically organic/molecular compounds, generally show very slow crystallization kinetics because of their rather cumbersome building blocks that need to be rearranged, while the corresponding driving forces per unit (or per mol) are not so high (intermolecular interactions via van-der-Waals forces are rather weak). So it seems that it is the unusual combination of low viscosity in the liquid, small building blocks, and significant driving forces (all not uncommon for inorganic materials), together with an extremely high fragility, that opens up a wide temperature window of low viscosity and thus, high crystallization speeds. How can a material have such a high fragility although it has no apparent indestructible and cumbersome building blocks?

Both switching speed and data retention of phase change memories are directly related to crystallization kinetics. For the first time, direct experimental evidence for crystal growth velocities reaches so far up into the fast regime, providing solid grounds for improved simulations of the switching processes in memories. On the low temperature side, our work makes apparent how much the stability against crystallization differs depending on whether it is determined in as-deposited or in melt-quenched amorphous phases. Our method is an ideal tool to investigate the technologically relevant phase. Furthermore, a careful consideration of the influence of structural relaxation is shown to be of great importance also for crystallization kinetics of phase change materials, not only for their electrical properties. Studying the viscosity of the amorphous phases will thus certainly impact the field of memory applications. However, this system, i.e. the combination of material class and experimental scheme, seems to be also highly instructive for a fundamental understanding of supercooled liquids and glasses in general.

REFERENCES

1.-54.: All references used above are identical to the ones given in the original publication of this work in *Nature Communications*, August 2013. For apparent spatial limitations here we refer the interested reader to this work, which is openly accessible as an online publication.

Biography

Martin Salinga is an academic staff member of the department of physics at RWTH Aachen University, Germany. He obtained his diploma in 2004 and his Ph.D. degree in 2008, both in physics, from RWTH Aachen. For his diploma thesis on crystallization kinetics of phase-change materials used in optical data storage, he performed his research both at RWTH Aachen and at Harvard University. From February 2005 until September 2006, he was on assignment at the IBM Almaden Research Center, investigating both crystallization kinetics and electronic properties of phase-change materials. Back at RWTH Aachen, Martin Salinga continues his studies on phase-change materials while also teaching (since June 2013 as “RWTH Lecturer”). Since July 2011 he is principal investigator and member of the steering committee of the collaborative research center “Nanoswitches”, a long-term research project funded by the German science foundation to study resistively switching chalcogenides for future electronics.