Glass Transition and Crystallization in Phase Change Materials

Martin Salinga[1*], Johannes Kalb[1], Michael Klein[1], Tobias Sontheimer[1], Frans Spaepen[2] and Matthias Wuttig[1]

[1]I. Physikalisches Institut der RWTH Aachen, 52056 Aachen, Germany
[2]Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA
*martin.salinga@physik.rwth-aachen.de

ABSTRACT

To fully exploit the potential of non-volatile memories employing phase change materials an in-depth understanding of crystallization kinetics is required. Hence both nucleation and growth rates need to be measured with high precision. We have determined the rates of nucleation and growth for different phase change materials including GeTe, AgIn-doped Sb_2Te and different GeSbTe compounds in the temperature range around 150°C. These experiments were performed combining Differential Scanning Calorimetry (DSC) and Atomic Force Microscopy (AFM). While DSC enables precise annealing cycles, the AFM provides superior spatial resolution to determine growth rates with high precision. The results show a remarkable difference in nucleation and growth for the different alloys. Classical theories on crystallization kinetics incorporate the reduced glass transition temperature (T_G/T_M). Using a special sample pre-treatment has enabled us to determine the glass transition temperature of phase change materials for the first time employing DSC. The data confirm that the glass transition temperature T_G is very close to the crystallization temperature T_C. The measured data for T_G (or T_C respectively) are compared with predictions of a model for the calculation of the glass transition temperature as a function of material composition. The comparison of experiment and theory helps to validate predictions of T_C based upon numerical approaches.

Key words: phase change materials, crystallization, glass transition, differential scanning calorimetry (DSC), atomic force microscopy (AFM), Germanium (Ge), Antimony (Sb), Tellurium (Te), thermal stability

1. INTRODUCTION

For several years already phase change materials are successfully used in optical data storage media like CD-RW, DVD-RW, HD-DVD, Blue-Ray-Disc [1]. In the more recent past another opportunity to capitalize on the very special properties of phase change materials is investigated intensively not only by universities but also by practically all major companies that are active in the electronic memory business [2, 3, 4, 5]. The goal is the development of non-volatile electronic memory devices, some of which employing probe storage techniques [6] others working with pillar- or line-shaped cell structures [7]. While the required properties of phase change materials differ from application to application, it is always important to know about the kinetics of crystallization of the chosen material both, if one wants to address the issue of data retention or discuss maximum data transfer rates. Especially approaches towards multi-level storage are based on a fine control over the degree of partial crystallization of a cell and by that strongly dependent on crystallization kinetics.

2. EXPERIMENTS, RESULTS & DISCUSSION

Crystal nucleation and growth:

In order to explore crystallization kinetics a method of sequential annealing and ex-situ measurement of the progress of crystallization is utilized. [8, 9] More specifically a differential scanning calorimeter (DSC) serves as a precise furnace for isothermal annealing of phase change thin films, which have been sputter-deposited on Silicon substrates. The thickness of the phase change layer is typically several tens of nanometers, so that the density contrast between the crystalline and the amorphous phase causes a significant reduction in height of crystalline areas compared to adjacent amorphous ones. This surface topography is detected by atomic force microscopy (AFM) between each annealing run. Figure 1 exemplarily shows

nucleation and growth of crystalline grains in a 40nm thick film of as-deposited amorphous $Ge_1Sb_2Te_4$ due to isothermal annealing at 95°C.

(a) 32 h (b) 32+4=36 h (c) 36+6=42 h

(d) 42+6=48 h (e) 48+4.5=52.5 h (f) height scale
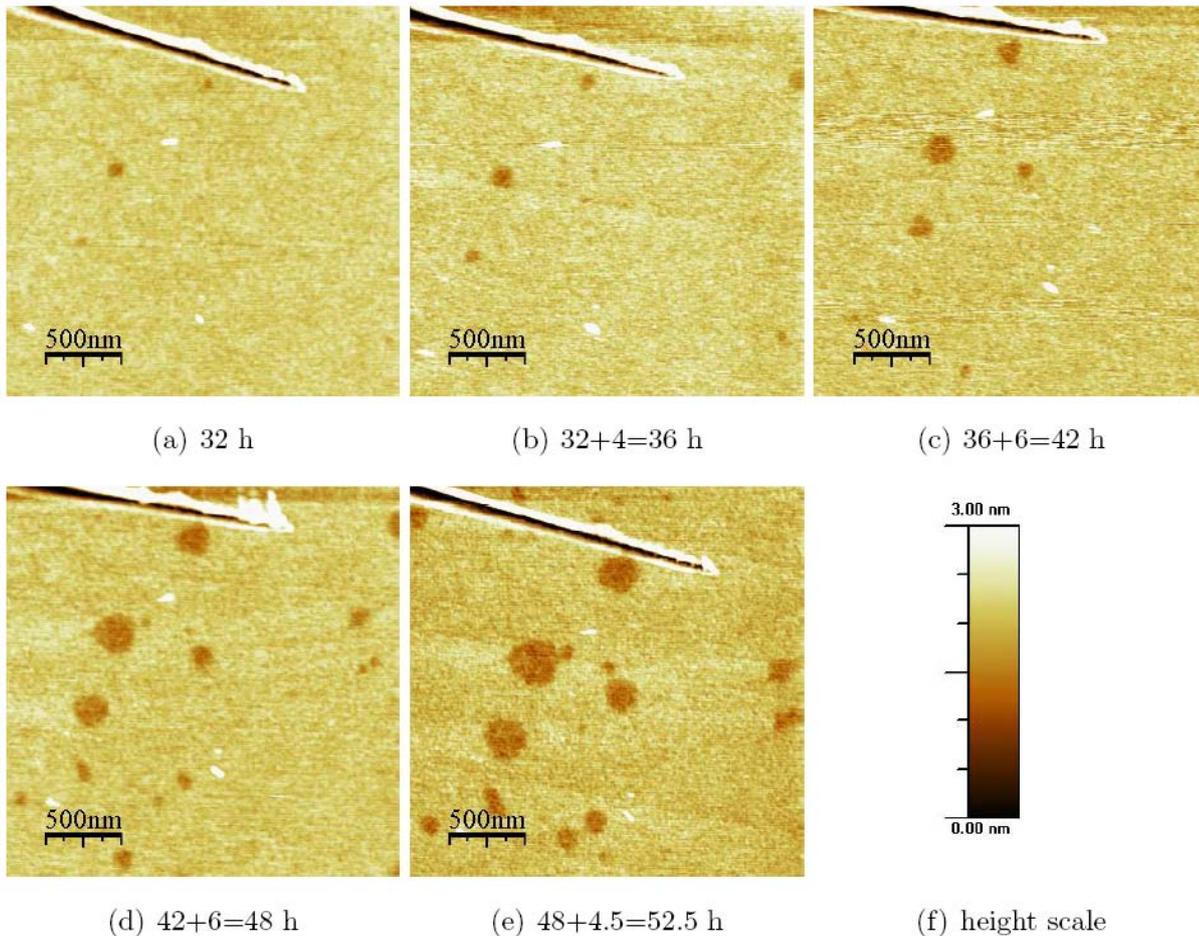
Figure 1: Nucleation and growth of crystalline grains (dark) in a 40nm thin film of amorphous as-deposited (bright) $Ge_1Sb_2Te_4$ on Silicon substrate after annealing at 95°C detected by atomic force microscopy. The dark mark at the top of the images serves to identify a specific position on the sample. [9]

From the changes in diameter of crystal grains detected with the AFM and the durations of isothermal annealing both crystal growth velocities and nucleation rates are determined for various temperatures. Figure 2 shows the resulting crystal growth velocities for several materials, $Ge_4Sb_1Te_5$, $Ge_2Sb_2Te_5$, $Ge_1Sb_2Te_4$, AgIn-doped Sb_2Te, $Ge_2Sb_1Te_4$ and GeTe, plotted in a logarithmic representation versus the reciprocal temperature. In the case of GeTe the observation of the progress of crystallization is not done with an AFM but with an optical microscope, because the latter is more suitable for the sizes of the crystalline grains in GeTe. The high precision of the furnace of the DSC both in time and in temperature allows for quite small errors of the experimental data. Without exception all materials show a strictly Arrhenius-like behavior in the investigated temperature ranges. This finding permits an extrapolation of the growth velocity to lower temperatures, i.e. below 100°C. The stability against recrystallization of small amorphous volumes that are surrounded by or at least in contact with crystalline regions is dominated by the crystal growth velocity as opposed to the nucleation rate. For such cases AgIn-doped Sb_2Te and $Ge_4Sb_1Te_5$ promise to provide for long data retention times, while $Ge_1Sb_2Te_4$ with an Activation barrier of only 1.89eV implies the highest probability of unintentional recrystallization at low temperatures.
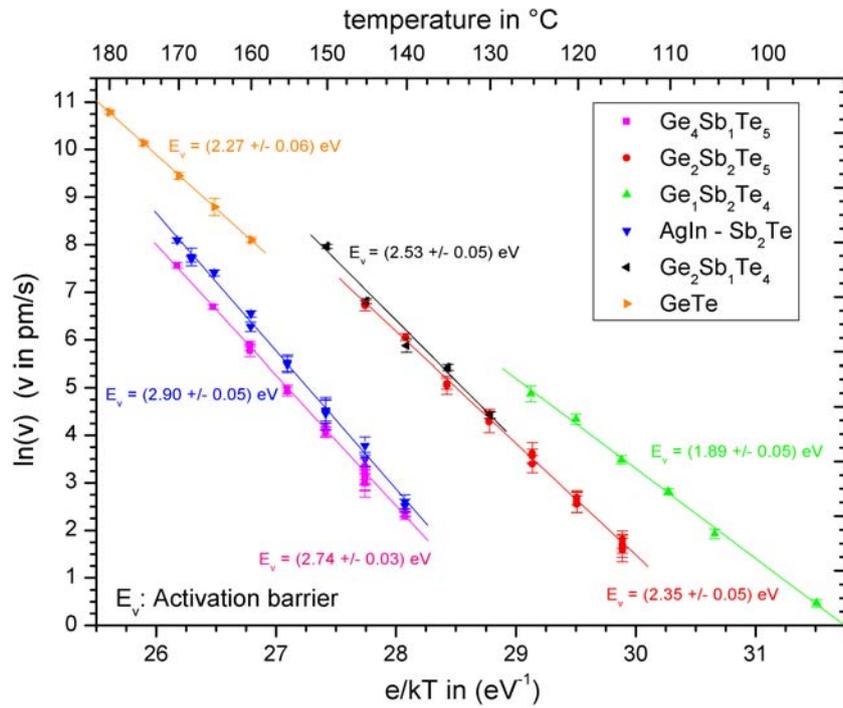
Figure 2: Dependance of crystal growth velocities v of various phase change materials on temperature. Activation barriers E_v are determined by fitting data with an Arrhenius-like behavior. Values are based on AFM measurements for all materials except of GeTe, in which case grains have been so large that crystallization could be best monitored by optical microscopy.
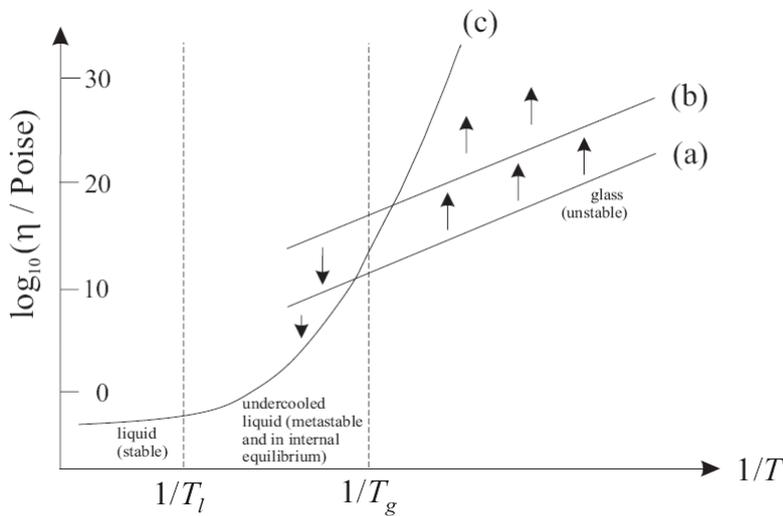

**Figure 3: Dependence of viscosity η on temperature for the liquid ($T > T_l$), for the undercooled liquid ($T_g < T < T_l$) and for different glass states ($T < T_g$). (a) Fast cooling. (b) Slow cooling. (c) Infinitively slow cooling. The glass states (a) and (b) show structural relaxation towards the undercooled liquid (c). [10]**

Crystallization and glass transition:

Both crystal nucleation rate and growth velocity increases with increasing diffusivity of the material, which following the Stokes-Einstein equation is inversely proportional to the viscosity. The dependence of the viscosity on temperature for a fragile glass former in the liquid, the undercooled liquid and the amorphous state respectively is shown in Figure 3. A priori it is not clear if crystallization takes place above or below the glass transition temperature Tg. In principle the glass transition should be observable in the heat flow signal of a DSC during heating up as an endothermic step due to the higher heat capacity of the undercooled liquid compared to the glass. Samples for this experiment are prepared by sputter depositing phase change materials on top of one of the following two possible substrates: PMMA covered SiO_2 glass substrates or thin plates of stainless steel. The 7 to 15 μm thick film is detached from its substrate in the first case by dissolution in Acetone and in the second case by bending the substrate. A single sample for the DSC experiment consists of about 5-10 mg of film fragments sealed in an Al pan. Figure 4 shows the heat flow during heating such samples with a constant rate for four different materials.
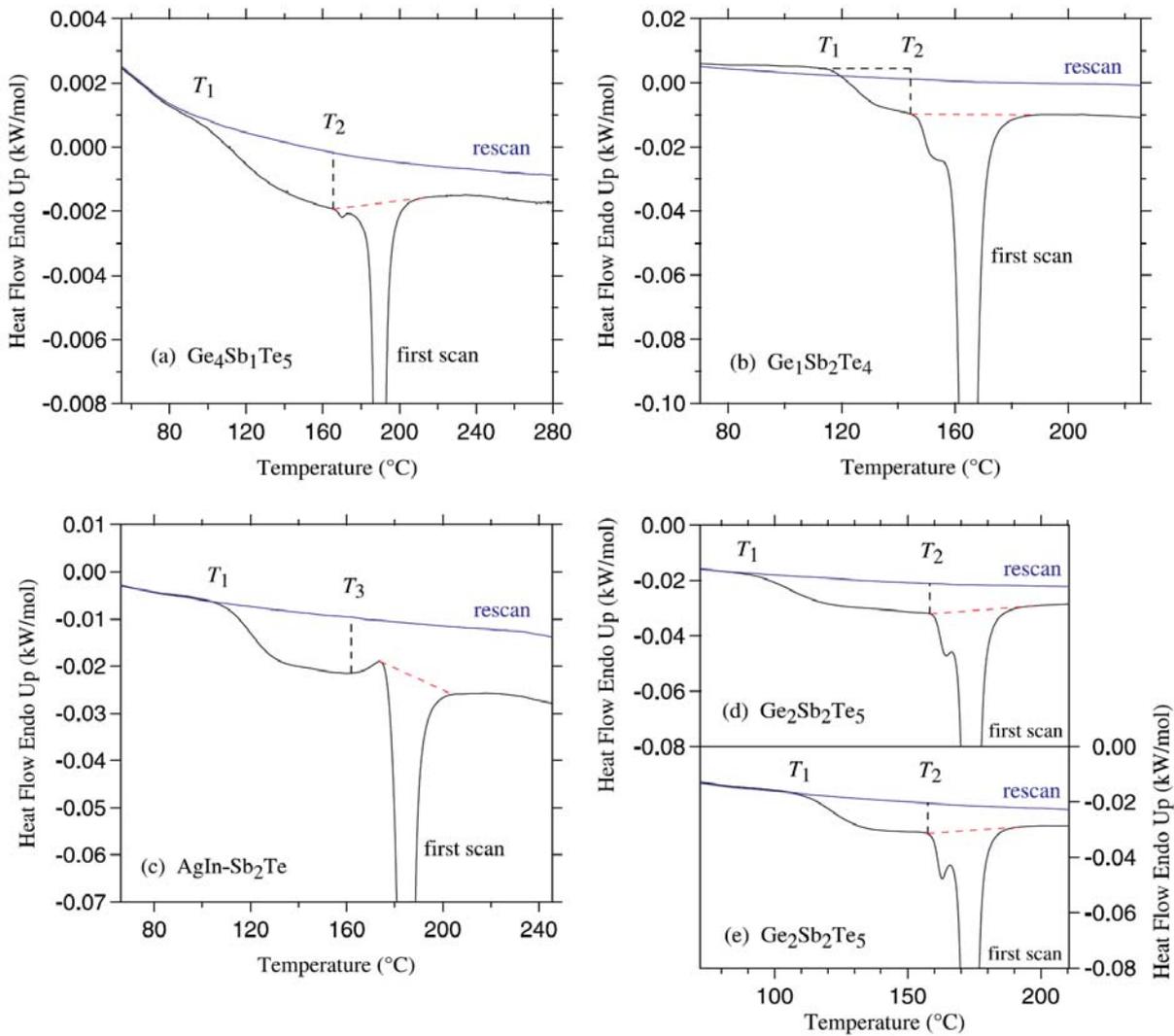
Figure 4: DSC signal: heat flow versus temperature for $Ge_4Sb_1Te_5$, $Ge_1Sb_2Te_4$, AgIn-Sb_2Te and $Ge_2Sb_2Te_5$. T_1 indicates the start of structural relaxation of the amorphous state. T_2 marks the onset of surface crystallization and T_3 the onset of the glass transition. Scan rate 40 K/min. [10]
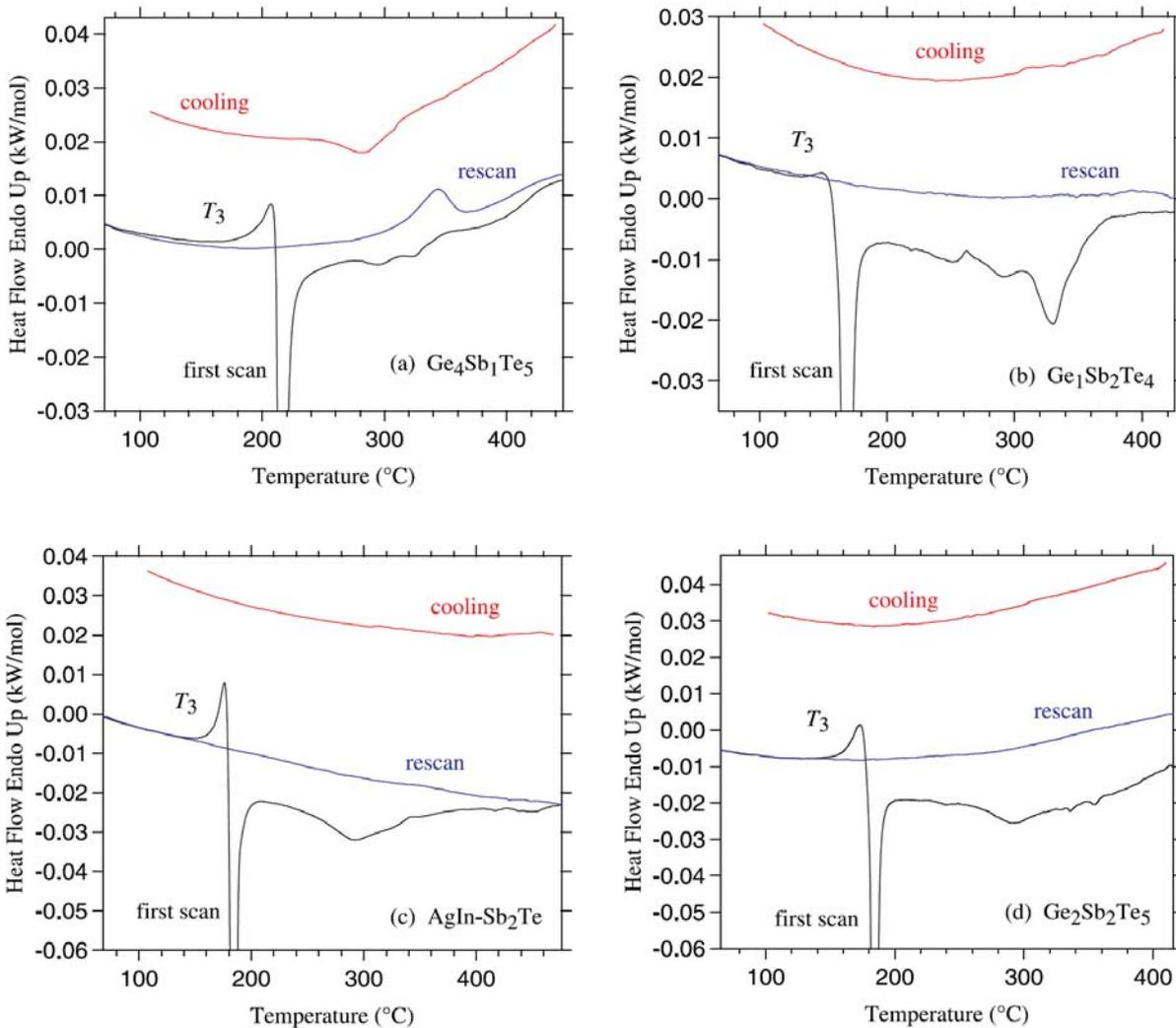
Figure 5: DSC signal: heat flow versus temperature for Ge$_4$Sb$_1$Te$_5$, Ge$_1$Sb$_2$Te$_4$, AgIn-Sb$_2$Te and Ge$_2$Sb$_2$Te$_5$ after pre-annealing for more than 40 hours. T$_3$ marks the onset of the glass transition. The scan rate is 40K/min. [10]

While for AgIn-doped Sb$_2$Te the onset of glass transition is observed shortly before the strong exothermic crystallization starts to dominate the heat flow signal, for all other phase change materials this measurement is performed on, i.e. Ge$_4$Sb$_1$Te$_5$, Ge$_1$Sb$_2$Te$_4$ and Ge$_2$Sb$_2$Te$_5$, crystallization takes place before any signal of a glass transition becomes visible. Careful measurement of the baselines allows for the identification of structural relaxation taking place in all four materials at elevated temperatures before crystallization or glass transition respectively. In order to separate the glass transition from crystallization, samples identical to the ones used for the experiments in Figure 4 have been pre-annealed well below crystallization temperature for around 40 hours. As indicated by the arrows in Figure 3 during an annealing below T$_g$ a glass structurally relaxes towards the undercooled liquid state increasing its viscosity. Afterwards the pre-annealed samples are heated at constant rate as in the measurements shown in Figure 4. The heat flow during these experiments is plotted versus temperature in Figure 5. In contrast to the as-deposited amorphous samples the pre-annealed ones show no structural relaxation anymore implying that even at temperatures higher than the pre-annealing temperature no further relaxation takes place on the timescale of the heating experiment. As the viscosity must have increased due to structural relaxation during pre-annealing, crystallization is inhibited and deferred towards higher temperatures. This opens a temperature window where the glass transition can be detected. And indeed after pre-annealing not only in AgIn-doped Sb$_2$Te but in all tested materials the onset of glass transition is observed (see T$_3$ in Figure 5). In principle the heat flow signal versus temperature should show an endothermic step accompanying the glass transition. In the case of the four materials investigated in this work, however, the completion of this ideal step function is interfered by the dominant exothermic crystallization peak briefly after the onset of the glass transition.

Prediction of glass transition temperatures:

In some memory applications a high crystallization temperature of the incorporated phase change material is desirable. For the design of such a new phase change material with higher crystallization temperature a method of predicting the influence of compositional variation is very attractive. To the knowledge of the authors, no such model exists in contrast to approaches to determine the glass transition temperature depending on the composition of an alloy. From the data presented above one can conclude that in phase change materials glass transition and crystallization take place in the same temperature range. So a model on the dependence of the glass transition temperature on stoichiometry is a legitimate approach to make predictions on compositional trends in the crystallization temperature of phase change alloys. A method for predicting the glass transition temperature based on composition, suggested by Lankhorst [11], can be described as follows: The hetero-nuclear bond enthalpy H_{AB} for a bond between elements A and B is calculated using Pauling's equation

$$H_{AB} = (H_{AA} + H_{BB})/2 + 96.14*(S_A - S_B)^\wedge 2,$$

where H_{AA} and H_{BB} are the homo-nuclear bond enthalpies and S_A and S_B are the electro-negativities of element A and element B, respectively. The values used for the electro-negativities, homo-nuclear bond enthalpies and number of valence electrons for the various elements are taken from Lankhorst as follows: S_{Ge}=2.01, H_{GeGe}=186 kJ/mol, N_{Ge}=4, S_{Te}=2.1, H_{TeTe}=197 kJ/mol, N_{Te}=6, S_{Sb}=2.05, H_{SbSb}=175 kJ/mol, N_{Sb}=5.

The algorithm determines the total bond enthalpy for a certain stoichiometry by using up the available valence electrons of the corresponding atoms forming the bond of highest enthalpy and giving preference to hetero-nuclear bonds over homo-nuclear ones. The coordination number for an element from groups VB and VIB is limited by the 8-N rule, leaving Sb with three and Te with two bonds per atom, while Ge always forms four bonds. The total bond enthalpy H_{tot} for a given composition is determined by summing up the bond enthalpies for all bonds formed in that composition:

$$H_{tot} = \sum_{A,B} n_{AB}*H_{AB},$$

where n_{AB} represents the number of bonds between atoms of elements A and B, while H_{AB} is the enthalpy of that bond. The glass transition temperature Tg (in K) is then calculated from the total bond enthalpy H_{tot} (in kJ/mol) using the empirical relationship.

$$Tg = 3.44*H_{tot} - 480.$$

Recently this method has been successfully used to predict the influence of Al- and Cu-doping on the crystallization temperature both of GeSb and SbTe. [12] Because phase change materials by definition show a very rapid crystallization, which makes it difficult to measure the glass transition, until now there has not yet been a comparison of predicted values for the glass transition temperature with experimental ones, but only with experimental values for the crystallization temperature. In order to compare the new experimental results on glass transition temperature with the simulation results, for $Ge_4Sb_1Te_5$, $Ge_1Sb_2Te_4$ and $Ge_2Sb_2Te_5$ the glass transition temperature has been calculated by using the method described above. In Figure 6 the onset temperatures of the glass transitions that are experimentally determined by differential scanning calorimetry (Figure 5) are plotted against those calculated values. It is evident that there is a discrepancy between the absolute numbers. Before, one could always argue that a difference between experimental crystallization temperature and modeled glass transition temperature is due to the physical difference between both transitions. Lankhorst himself claimed that glass transition temperatures of 350 K for $Ge_1Sb_2Te_4$ and of 384 K for $Ge_2Sb_2Te_5$ are well in line with the experimentally determined crystallization temperatures of 412 K for $Ge_1Sb_2Te_4$ and 433 K for $Ge_2Sb_2Te_5$. [11] Facing the new experimental evidence on glass transition temperatures, one has to state that the absolute results of the algorithm do not match reality very well. However, it is remarkable how well experimental and theoretical data follow a linear correlation. In view of the fact that the used algorithm itself contained as its last step an empirical linear relationship between the calculated total enthalpy of atomization and the glass transition temperature, one simply adapting the parameters of this linear relationship to the GeSbTe system according to the linear fit plotted in Figure 6 is reasonable. If this rather easy fix of the discrepancy between model and experiment will work also for other compounds from the GeSbTe system or if a major change of the model is necessary, has to be investigated.
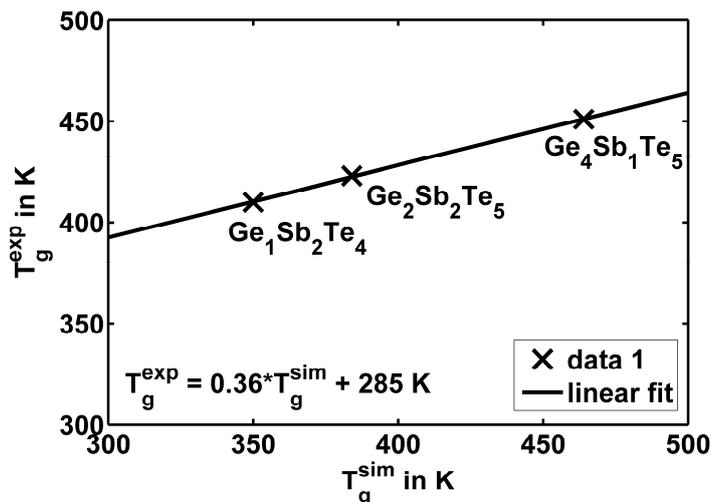
Figure 6: Glass transition temperatures: Comparison between experimental and predicted values for the three different alloys from the GeSbTe system investigated by differential scanning calorimetry.

4. CONCLUSION

Measurements of crystallization kinetics at moderate temperatures for six different phase change materials are compared. The strict Arrhenius behavior of these results allows extrapolations of the experimental values to low temperatures in order to calculate the stability of amorphous volumes against crystallization. In application this stability is directly linked to retention times. To design new phase change materials with higher thermal stability a model for predicting the glass transition temperature is tested on fast phase change materials. Forcing alloys from the GeSbTe system to structurally relax in the amorphous state preceding a thermal analysis with a DSC revealed the glass transition temperature of these alloys that is otherwise not detectable due to crystallization. These experimental results are used for the first time to compare predicted values of the glass transition temperature with experimental ones for fast crystallizing phase change materials. The comparison shows that an adaptation of the theoretical model is necessary.

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Biography

Martin Salinga received his diploma in physics from RWTH Aachen, Germany, end of 2004. He did the one year research for his diploma thesis with the topic "Kinetics of fast nucleation and growth processes in Tellurium alloys" both at the I. Institute of Physics A of RWTH Aachen and at the Department of Engineering and Applied Sciences of Harvard University advised by Professor Matthias Wuttig and Professor Frans Spaepen respectively. From February 2005 till September 2006 Martin Salinga worked at the IBM Almaden Research Center in San Jose, California, on crystallization kinetics and electronic properties of phase change materials. Back at the RWTH Aachen since October 2006 he is continuing his studies in this field as a PhD student in solid state physics.