Resolving glass transition in Te-based phase-change materials by modulated differential scanning calorimetry

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Glass transitions of Te-based phase-change materials (PCMs) were studied by modulated differential scanning calorimetry. It was found that both Ge2Sb2Te5 and GeTe are marginal glass formers with ΔT (= Tg − Tc) less than 2.1 °C when the heating rate is below 3 °C min−1. The fragilities of Ge2Sb2Te5 and GeTe can be estimated as 46.0 and 39.7, respectively, around the glass transition temperature, implying that a fragile-to-strong transition would be presented in such Te-based PCMs. The above results provide direct experimental evidence to support the investigation of crystallization kinetics in supercooled liquid PCMs. © 2017 The Japan Society of Applied Physics

Phase-change materials (PCMs) are commonly used in rewritable optical memory and/or electronic non-volatile devices owing to the reversible transition from the amorphous (high resistivity and low reflectivity) to crystalline phase (low resistivity and high reflectivity). Compared with the ongoing improvements in other memories, the data transfer speed of phase-change memory should be improved continuously.1 It is well known that understanding the crystallization kinetics of PCMs is necessary to improve their data transfer speed, and related topics have been widely investigated using various experimental tools and computer simulations.2–5) Nevertheless, a quantitative study of the crystallization kinetics in supercooled liquid requires the knowledge of fundamental thermal properties, such as peak crystallization temperature (Tc) and melting temperature (Tm), as well as glass transition temperature (Tg). Generally, Tc and Tm of PCMs are easily determined owing to a large enthalpy change in crystallization and melting processes. However, it is always challenging to obtain Tg experimentally because of the weak glass transition behavior, which is usually overlapped by the strong crystallization and/or relaxation signal in PCMs.

Recently, various methods have been employed to investigate the crystallization kinetics for PCMs, such as ultrafast calorimetry,2–6) dynamic transmission electron microscopy,7) laser irradiation,8,9) and electrical pulse heating.10) A viscosity model, namely, the Mauro–Yue–Ellison–Gupta–Allan (MYEGA) model based on the temperature-dependent configurational entropy,11) has been developed to study the crystallization kinetics. There are three parameters in the MYEGA model, i.e., fragility (m), Tg, and viscosity at infinite temperature (η∞). It has been reported that a convergence of η∞ at the particular value of 10−2.9 Pa s12) has physical meaning in terms of the constraint theory description.13) Thus, the MYEGA model can be considered as a two-parameter model in which the determination of m would be strongly influenced by Tg. It has been reported that the parameters of the crystallization kinetics, such as fragility, viscosity, and crystal growth rate, cannot be accurately estimated owing to the uncertain Tg.14) Therefore, it is highly desired to determine Tg in order to study crystallization kinetics.

Numerical simulations have been used to estimate Tg in PCMs in the last two decades. For instance, a Tg of 400 °C was calculated for Ge2Sb2Te5 (GST).15) Hudgens and Johnson claimed that GST has a Tg of 350 °C.16) Compared with the onset temperature of crystallization (Tc), which is ~150 °C for GST,17,18) these values of Tg seem to be overestimated, because the Tg of the material is always lower than its Tc. A model based on the correlation between Tg and the enthalpy of atomization was presented for estimating the Tg of a covalent amorphous material.19) It showed that Tg was 111 °C for GST, which seems reasonable. However, Tg was estimated as 228 °C for GeTe, which is higher than its Tc of ~180 °C.20) On the other hand, experimental results were also obtained to investigate the glass transition in PCMs. For instance, by impedance and calorimetry measurements, the Tg for GST was reported as ~100 °C.21) However, the signal-to-noise ratio of the data is not good enough to be considered as strong evidence. Kalb et al. tried to detect the Tg signal in some Te-based PCMs via conventional differential scanning calorimetry (DSC).22) Nevertheless, no thermal signal of Tg was observed in the temperature range below its Tc at the heating rate from 5 to 80 °C min−1. In their subsequent study, however, an endothermic signal of Tg before Tc was found after prolonged relaxation.23) The result showed that Tg is ~10 °C less than the crystallization temperature when the heating rate is 40 °C min−1. Obviously, the determination of Tg in PCMs is still ambiguous and controversial.

Kalb et al. indicated that the weak glass transition in PCMs would be overlapped by relaxation and/or crystallization.22,23) It also implies that the conventional DSC is not a good choice for detecting such an overlapped and complex transition directly. Modulated DSC (mDSC) is a new development of DSC in which a small sinusoidal modulation is superimposed on the linear temperature ramp. A discrete Fourier transform algorithm is applied to the resultant data to...
GeTe targets, respectively. For every deposition, the base and which is equal to the heat transition and crystallization in the reversing (red) and nonreversing (blue) modulated temperature programs. This generates an output as “modulated heat flow”, which can be separated into two components, i.e., reversing and nonreversing heat flows. Glass transition is a reversing component, but relaxation and crystallization are nonreversing components. Therefore, mDSC can be utilized to separate the weak glass transition signal from the overlapped and complex heat flow.

In this work, we have investigated the glass transition in Te-based PCMs (GST and GeTe) using mDSC. It was found that is very close to in PCMs, and smaller than 2.1 °C when the heating rate is below 3 °C min⁻¹, implying that they are marginal glass formers. Moreover, together with the conclusion of Kalb et al., a linear fitting can be applied to yield the GST and GeTe fragilities of 46.0 and 39.7, respectively, around . The standard values for GST and GeTe were also extrapolated as 167 and 187 °C, respectively.

Amorphous GST and GeTe films were deposited on SiO₂/Si(100) by magnetron sputtering using single GST and GeTe targets, respectively. For every deposition, the base and working pressures were set to −4 × 10⁻⁶ and 0.35 Pa, respectively. The film thicknesses were 3 μm for GST and 2 μm for GeTe. The stoichiometry was confirmed by energy dispersive spectroscopy (EDS). Amorphous samples of 5 ± 1 mg weight were sealed in aluminum pans. Total, reversing, and nonreversing heat flow measurements were carried out using a NETZSCH instrument DSC204F1 calorimeter.

Figure 1 shows mDSC results for as-deposited GST, including total, reversing, and nonreversing heat flows. Apparently, no endothermic signal can be found in the total heat flow. However, by the specific function of separating an overlapped signal in mDSC, an obvious endothermic signal, which is ascribed to the glass transition, can be observed in the separated reversing heat flow. The corresponding onset temperature of the endothermic peak is determined to be 159.3 °C. The crystallization signal can be easily found in both total and nonreversing heat flows. It is more reasonable to estimate at 161.7 °C from the nonreversing heat flow because the crystallization is a nonreversing process. Therefore, the parameter , which is defined as , is only 2.4 °C for GST at a continuous heating rate of 3 °C min⁻¹. This implies that GST is a marginal glass former with a high crystallization speed. This is an important factor for screening a material that is useful for fast phase-change recording. In addition, a weak exothermic peak at ~149 °C is presented in the total and nonreversing heat flows. It can be observed clearly from the intensity-enhanced nonreversing heat flow in the left bottom in Fig. 1. This is ascribed to natural oxidation and results in the heterogeneous nucleation at the sample surface. It has been confirmed from the results of transmission electron microscopy that naturally oxidized Ge–Sb–Te alloys crystallize prior to the rest of the film. Such weak crystallization behavior has also been reported by Kalb et al. More interestingly, the endothermic signal in the reversing heat flow exhibits two peaks that are related to the amorphous structural evolution in a continuous heating process. The first endothermic peak is ascribed to the intrinsic signal of glass transition, while the second endothermic peak is due to the accompanying crystallization when the glass transition occurs simultaneously. This complicated process will be discussed in detail in future work.

We repeated the measurements and obtained similar results, confirming the reliability of the experiments. Such measurements were also carried out using other heating rates, i.e., 1 and 2 °C min⁻¹, and the results are shown in Figs. 2(a) and 2(b). The endothermic signal for glass transition can be observed in each reversing heat flow. The glass transition of GeTe was also studied by mDSC. As depicted in Figs. 2(c) and 2(d), values for GeTe are 172 and 175.8 °C at heating rates of 1 and 2 °C min⁻¹, respectively. The corresponding characteristic temperatures with errors are listed in Table I.

Figure 3 shows the DSC traces for GST and GeTe at a heating rate of 40 °C min⁻¹. At such a high heating rate, the modulated model cannot reveal the weak glass transition in PCMs. Thus, here, we only employed the conventional model (linear heating) to detect the heat flow change during continuous heating. It can be seen that is 180.1 and 200.8 °C for GST and GeTe, respectively. However, no endothermic signal of glass transition can be observed. For PCMs, Kalb et al. suggested that at a heating rate of 40 °C min⁻¹ can be determined as 10 °C below their . Therefore, the values of at 40 °C min⁻¹ for GST and GeTe can be inferred as 170.1 and 190.8 °C, respectively. Similar results were obtained in repeated measurements. Such characteristic temperatures with errors and corresponding calorimetric parameters are listed in Table I. As we can see, all the characteristic temperatures increase with the increase in heating rate. The parameter , which is a criterion to judge the glass forming ability, is only 1.8 and 2.1 °C for GeTe at heating rates of 1 and 2 °C min⁻¹, and 0.6 to 2.0 °C for GST when the heating rate increases from 1 to 3 °C min⁻¹. Such small indicates that these Te-based PCMs are marginal glass formers with a high crystallization speed, and thus are promising for fast phase-change memory. Moreover, the enthalpy changes that include the glass transition enthalpy and the crystallization enthalpy of GST and GeTe were calculated and the results are listed in Table I. It was found that increases with increasing heating rate, but remains almost constant for both GST and GeTe.
We plotted $\ln \varphi$ vs $1/T_g$ and the results are shown in Fig. 4. Note that the $T_g$ at 40 °C min$^{-1}$ was estimated by the method suggested by Kalb et al. Apparently, there is an excellent linear relationship with a good quality of fit ($R^2 > 0.996$) between $\ln \varphi$ and $1/T_g$ for both GST and GeTe, implying that their conclusion strongly supports our experimental results. The fragility ($m$) can be obtained by determining the activation energy $E_a$ at $T_g$ and taking the slope of $E_a/R$. It yields $m = E_a/(\ln 10 \times T_g \times R)$, where $T_g$ is the standard glass transition temperature that is determined at a heating rate of 20 °C min$^{-1}$. Note that the standard $T_g$ cannot determine.
be obtained directly here, but it can be extrapolated as 167 and 187 °C for GST and GeTe, respectively, using the Arrhenius plots. Thus, the fragility \( m \) can be estimated as 46.0 ± 1.17 and 39.7 ± 0.84 for GST and GeTe, respectively. However, on the basis of the ultrafast DSC, Orava et al. reported that \( m \) is ~90 for GST,23 and our previous study showed \( m \) of GeTe of ~130.25) Apparently, the present results of the fragility of PCMs are different from the previous ones. It may due to the fragile-to-strong transitions present in such Te-based supercooled liquids. A similar situation has been reported in Ag–In–Sb\(_2\)Te,3) which exhibits an obvious fragile-to-strong transition with two kinds of temperature-dependent viscosity in the temperature range from \( T_g \) to \( T_m \). The fragility \( m \) deduced from the weak dependence at low temperature from \( T_g \) to \( T_m \) (the temperature of the fragile-to-strong transition) is 37,3) while the fragility \( m' \) from the strong dependence at high temperature from \( T_m \) to \( T_g \) is 135.9) The fragile-to-strong transition magnitude (\( \Delta f \)) is determined by \( \Delta T \) of 2.1 °C when the heating rate is 3 °C min\(^{-1}\) for GST and \( \Delta T \) of 2.1 °C when the heating rate is 2 °C min\(^{-1}\) for GeTe. These results confirmed that such Te-based PCMs are marginal glass formers that are useful for ultrafast phase-change recording. Furthermore, Arrhenius plots of ln \( f \) vs 1/\( T_g \) yielded \( m \) values of 46.0 and 39.7 for GST and GeTe, respectively, around \( T_g \). Compared with the previous reports, \( m \) at a high temperature range is larger than that in this work. This is attributed to the unrevealed fragile-to-strong transition in supercooled liquid GST and GeTe, and we estimated that the transition magnitudes \( f \) are 1.9 and 3.3 for GST and GeTe, respectively.

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