

# **Structural, optical and mechanical stress measurements upon crystallization of phase change materials\***

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## Abstract

Mechanical stress measurements as well as an investigation of optical and structural properties was performed during crystallization of different phase change materials. Upon crystallization a considerable stress build up is observed, which scales with the volume change upon crystallization. Nevertheless the observed stress change only corresponds to approximately 9% of the stress estimated for a purely elastic transformation. Further evidence for stress relief phenomena comes from the temperature dependence of the stress in the crystalline and amorphous states.

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In phase change recording the reversible transformation between an amorphous and a crystalline state is employed to write and erase information. The optical contrast between the amorphous and crystalline state of the material, which is usually a ternary or quaternary Te alloy, enables a straightforward reading of the information. The difference in optical properties is essential to obtain a high contrast between amorphous and crystalline regions. The change of optical properties is accompanied by a change of structural properties. The characterization of this structural change is of vital importance for an in-depth understanding of the kinetics of crystallization and amorphization. As already pointed out by several groups it is essential for a fast phase transformation that melting of the phase change media occurs without phase separation. Furthermore the crystalline phase should have a simple structure, such as e.g. a cubic or hexagonal atomic arrangement. While we already have a fairly good understanding of optical and structural properties of phase change materials much less effort has been devoted to a characterization of mechanical properties. These properties will be the focus of this presentation. It will be shown that stress measurements during crystallization enable a deeper understanding of the mechanism of crystallization and crucial material limits.

The phase transformation between the amorphous and crystalline state is accompanied by a considerable volume change. This is demonstrated in fig. 1 for three different phase change alloys, where the relative film thickness is shown after annealing for 10 min. to different temperatures. The films, which had thicknesses between 35 and 60 nm were sputter deposited onto Si wafers. To facilitate the comparison of the data, the thickness, which has been measured by X-ray reflectometry to better than 1 Å (0.2 – 0.3%) is normalized with respect to the thickness of the as-deposited film. For the three different alloys studied here, crystallization proceeds around 155°C for AgInSbTe (Ag 5.5%, In 6.5%, Sb 59%, Te 29% as determined by inductively coupled plasma emission spectroscopy and energy dispersive X-ray analysis), 130°C for Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> and 170°C for Ge<sub>4</sub>Sb<sub>1</sub>Te<sub>5</sub>. In all cases crystallization is accompanied by a considerable reduction in film thickness. The smallest thickness decrease of 5.5% is observed for AgInSbTe, while Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> shows a 6.5% thickness decrease upon crystallization. Ge<sub>4</sub>Sb<sub>1</sub>Te<sub>5</sub> is even characterized by a 9.0% thickness reduction.

These changes in film thickness will lead to pronounced mechanical stresses in the films and could even cause severe limitations for the cyclability of the material, if these stresses are relieved by viscous flow. Indeed it has been shown that the cyclability of phase change media can be improved if oxygen or nitrogen atoms, which are argued to suppress the flow of the active layer, are added to the phase change film [1]. We have observed such stress induced effects also in atomic force microscopy (AFM) images of crystalline bits, which were produced by a pulse of a focussed laser [2]. While AFM shows that upon laser irradiation a well defined circular area is crystallized, it also reveals that nanometer sized cracks are formed in the crystalline film, which presumably are formed to reduce the film stress. Unfortunately from such rather qualitative observations, however, no quantitative information on the local film stress can be obtained. Therefore we employ a different technique to precisely determine the film stresses upon crystallization.

Wafer curvature measurements [3] are employed to determine the stress induced by crystallization in thin films of phase change material sputter deposited onto thin glass, Si or sapphire substrates. The wafer curvature is measured by a laser scanning technique using a rotating mirror. The position sensitive detector additionally enables the determination of the reflectance change upon crystallization. Hence we can simultaneously monitor the stress change and the optical reflectance change upon crystallization. The stress change is determined from Stoney's equation [4]

$$\Delta\sigma = \frac{1}{6} \left( \frac{E_s}{1-\nu_s} \right) \frac{t_s^2}{t_f} \left( \frac{1}{R} - \frac{1}{R_0} \right) \quad (1)$$

where  $E_s / 1 - \nu_s$  is the biaxial elastic modulus of the substrate,  $t_s$  and  $t_f$  denote the thickness of the substrate and the film, respectively and  $\frac{1}{R_0}$  and  $\frac{1}{R}$  are the curvature of the substrate at room temperature and after heating to a temperature  $T$ ,

respectively. For a quantitative analysis of the stress, the film thickness has been determined with high precision by X-ray reflectometry. In fig. 2 examples for the crystallization upon annealing of three different phase change films are shown. Fig. 2(a) displays the reflectance (top portion) and the mechanical stress (lower portion) for a 150  $\mu\text{m}$  thick glass substrate covered by 85 nm of AgInSbTe. Upon heating above 160°C (heating rate 3 K/min), a pronounced change in reflectance is observed. Once the reflectance has increased by 35 % after heating above 170°C, it remains virtually constant even after subsequent cooling down to room temperature. This reflectance change is characteristic for crystallization as confirmed by X-ray diffraction measurements. Correlated with the phase transition is a stress change of 105 MPa. Further heating of the sample leads to a reduction in film stress. Neither the rapid stress build up upon heating above 160°C nor the subsequent stress decrease upon further heating are reversible. This can be seen from the stress data upon cooling down to room temperature. Subsequent heating back to 200°C leads to a reversible change of film stress, which is attributed to the different coefficients of thermal expansion of the film and the substrate. By comparing the reversible stress change upon heating or cooling for films deposited onto different substrates we have determined the coefficient of thermal expansion and the biaxial elastic modulus ( $M_f = E_f / 1 - \nu_f$ ) for the different phase change materials studied here. The corresponding data which were obtained by measuring the stress change on thin Si wafers and glass substrates are compiled in tab. I. While the coefficient of thermal expansion for the crystalline phase varies between  $1.50 \times 10^{-5}/\text{K}$  for AgInSbTe,  $1.81 \times 10^{-5}/\text{K}$  for  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  and  $1.99 \times 10^{-5}/\text{K}$  for  $\text{Ge}_4\text{Sb}_1\text{Te}_5$ , respectively, the biaxial elastic modulus for the crystalline phase ranges from 53 GPa for AgInSbTe to 50 GPa for  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  and 47 GPa for  $\text{Ge}_4\text{Sb}_1\text{Te}_5$ . Similar values are also obtained for the amorphous phase. With these numbers in hand we can estimate the stress change upon crystallization assuming that the process

proceeds elastically. Under this condition [5] the stress change is  $\Delta\sigma = -M_f \frac{1 - \nu_f}{1 + \nu_f} \epsilon_{zz_{total}}$ , where  $\nu_f$  is the Poisson ratio

and  $\epsilon_{zz_{total}}$  the total expansion in z-direction. The latter has been determined by X-ray reflectometry, as displayed in fig. 1, while  $M_f$  is derived from the reversible stress change upon heating and cooling for different substrates and  $\nu_f$  is assumed to be 0.3, a value typical for many materials including chalcogenides. The stress change for an elastic process is now determined to 1.5 GPa for AgInSbTe, 1.7 GPa for  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ , and 2.3 GPa for  $\text{Ge}_4\text{Sb}_1\text{Te}_5$ . The measured stress change is much smaller, however, and corresponds to 105 MPa for AgInSbTe, 165 MPa for  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  and 215 MPa for  $\text{Ge}_4\text{Sb}_1\text{Te}_5$ . Hence, only a fraction of approximately 9% of the calculated stress change assuming elastic behaviour is found for the different films studied here. This clearly demonstrates that a considerable fraction of the stress in the phase change film is relieved by plastic flow in the amorphous phase. This is supported by a comparison with the observed rate of the stress change of the crystalline phase. In Figure 2(a) it can be seen, that upon annealing of the crystalline phase for 5 min. at

200°C, the stress relaxation rate is very small compared to the rate of stress relief that occurs within 100s upon crystallization. This implies, that the inelastic stress change must be accommodated by viscous flow in the amorphous phase and not in the crystalline phase. For an application of phase change materials for reversible optical data storage a small volume change and a small elastic modulus are clearly preferred to avoid extensive stress build up and the resulting viscous flow of the material upon crystallization.

Further information on the mechanism of stress formation comes from a comparison with data obtained for films with a thin dielectric layer on top of the phase change material. The influence of thin capping layers on phase change kinetics has already been addressed in several studies [6-8]. The simultaneous detection of mechanical stresses, however, has the tremendous advantage of enabling fast and unequivocal insight into the crystallization mechanism. This is displayed in fig. 3 (closed circles), where a 61 nm thick  $\text{Ge}_4\text{Sb}_1\text{Te}_5$  sample with a thin (~ 1 nm) native oxide is investigated. Compared with the data in fig. 2(c), two important differences are evident. The optical reflectance change already takes place at a considerably lower temperature, i.e. 162°C as compared with 182°C for the unoxidized film. This is evidence that the crystallization proceeds via heterogeneous nucleation at the interface between the oxide and the phase change film. The onset of crystallization is accompanied by a small stress change, but the major stress change is only observed after the reflectance change is almost complete. This implies that a large fraction of the stress is only formed when different grains start to form a continuous crystalline film. Such a scenario is indicative for a high viscous flow rate of the amorphous phase, which reduces the maximum film stress that can be observed. This is supported by annealing and cooling cycles for the amorphous phase below the crystallization temperature, which show an irreversible stress change. Further experiments are in progress to measure the viscosity of the amorphous films. The scenario of interface driven heterogeneous crystallization, however, can be confirmed by a straightforward experiment. Turning the sample upside down, the laser beam passes through the glass substrate onto the PC film. This geometry leaves the stress measurement unaffected, but leads to a rather different reflectance change (open circles), since now the laser beam has to first pass through the amorphous  $\text{Ge}_4\text{Sb}_1\text{Te}_5$  film, so that the onset of crystallization at the interface is not visible. This directly confirms the heterogeneous crystallization process at the oxide/phase change interface presented above.

In summary we have shown that mechanical stress measurements provide crucial information on the crystallization mechanism in thin phase change layers and possible material limitations. The determination of the temperature dependence of film viscosity from stress measurements could provide further insight into the kinetics of crystallization processes in phase change materials.

## Figures

Fig. 1 Film thickness of AgInSbTe, Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> and Ge<sub>4</sub>Sb<sub>1</sub>Te<sub>5</sub> films as a function of increasing annealing temperature as measured by X-ray reflectometry. Crystallization, which leads to a sudden decrease in film thickness, is observed at 155°C for AgInSbTe, 130°C for Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> and 170°C for Ge<sub>4</sub>Sb<sub>1</sub>Te<sub>5</sub>. The more gradual thickness change upon annealing for Ge<sub>4</sub>Sb<sub>1</sub>Te<sub>5</sub> is partly due to the formation of a thin oxide film. To facilitate a comparison of different data sets, all thicknesses are normalized with respect to the thickness of the as-deposited film. Crystallization leads to a 5.5% thickness decrease for AgInSbTe, a 6.5% thickness decrease for Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> and a 9% thickness reduction for Ge<sub>4</sub>Sb<sub>1</sub>Te<sub>5</sub>.

Fig. 2 Stress and reflected intensity from (a) 85 nm AgInSbTe on a 150 μm glass substrate, (b) 85 nm Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> on a 200 μm Si wafer and (c) 61 nm Ge<sub>4</sub>Sb<sub>1</sub>Te<sub>5</sub> on a 200 μm Si wafer. For all materials studied here the reflectance change upon crystallization is accompanied by an irreversible stress change. Irreversible stress changes are also observed for the data in (a) and (b) where a considerable stress reduction is observed upon annealing for 5 minutes at 200°C. From the stress change upon subsequent cooling down to room temperature the coefficient of thermal expansion and the biaxial modulus have been determined.

Fig. 3 Stress and reflected intensity from a 61 nm Ge<sub>4</sub>Sb<sub>1</sub>Te<sub>5</sub> film on a 150 μm glass substrate. The phase change film is covered by a 1 nm thin oxide film. This leads to a pronounced shift of the transition in reflection but not in the stress measurement. Measurements from the sample backside, i.e. through the glass substrate on the interface between the phase change film and the substrate show a delayed change in reflectance (open circles) but the same stress measurement (not shown). This shows that the oxide layer leads to heterogeneous crystallization at the film surface, which then grows towards to substrate.

References:

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Table I. Coefficient of thermal expansion and biaxial modulus  $M_f$  obtained from stress measurements for phase change films on different substrates.  $\epsilon_{zz \text{ total}}$  describes the total change in film thickness upon crystallization, while  $\Delta\sigma_{\text{elast}}$  is the expected stress change upon crystallization assuming elastic behaviour. The observed stress change is denoted as  $\Delta\sigma_{\text{exp}}$ .

	$\alpha$ ( $10^{-5}/\text{K}$ )	$M_f$ (GPa)	$\epsilon_{zz \text{ total}}$ (%)	$\Delta\sigma_{\text{elast}}$ (GPa)	$\Delta\sigma_{\text{exp}}$ (GPa)
AgInSbTe	$1.50 \pm 0.04$	$53 \pm 1$	$-(5.5 \pm 0.2)$	1.5	0.105
Ge <sub>2</sub> Sb <sub>2</sub> Te <sub>5</sub>	$1.81 \pm 0.06$	$50 \pm 2$	$-(6.5 \pm 0.2)$	1.7	0.165
Ge <sub>4</sub> Sb <sub>1</sub> Te <sub>5</sub>	$1.99 \pm 0.18$	$47 \pm 4$	$-(9.0 \pm 0.3)$	2.3	0.215

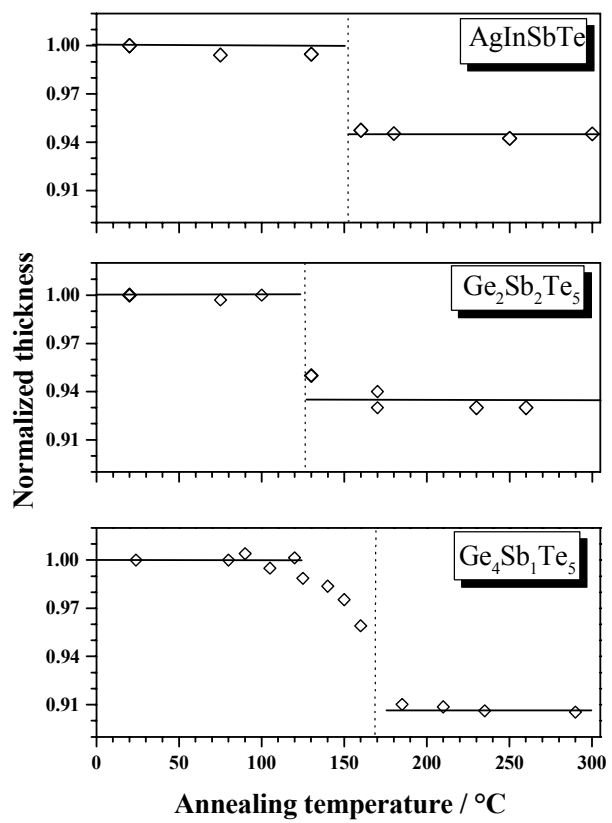


Figure 1



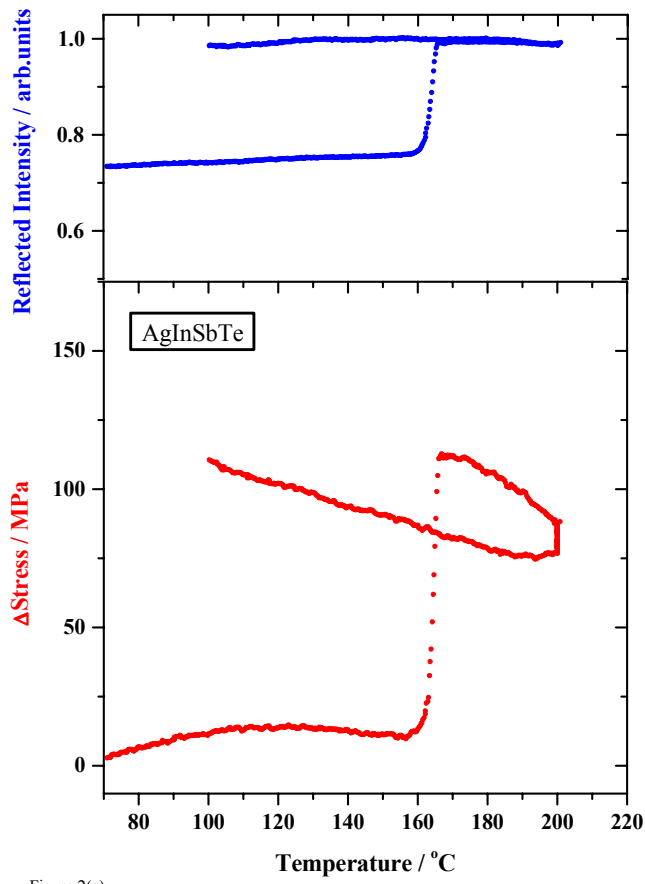


Figure 2(a)

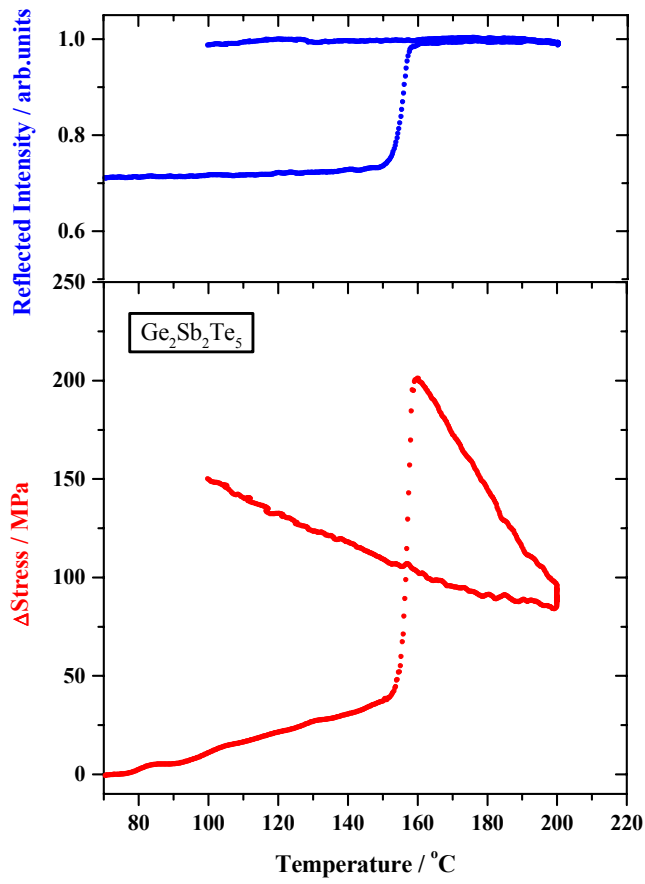


Figure 2(b)

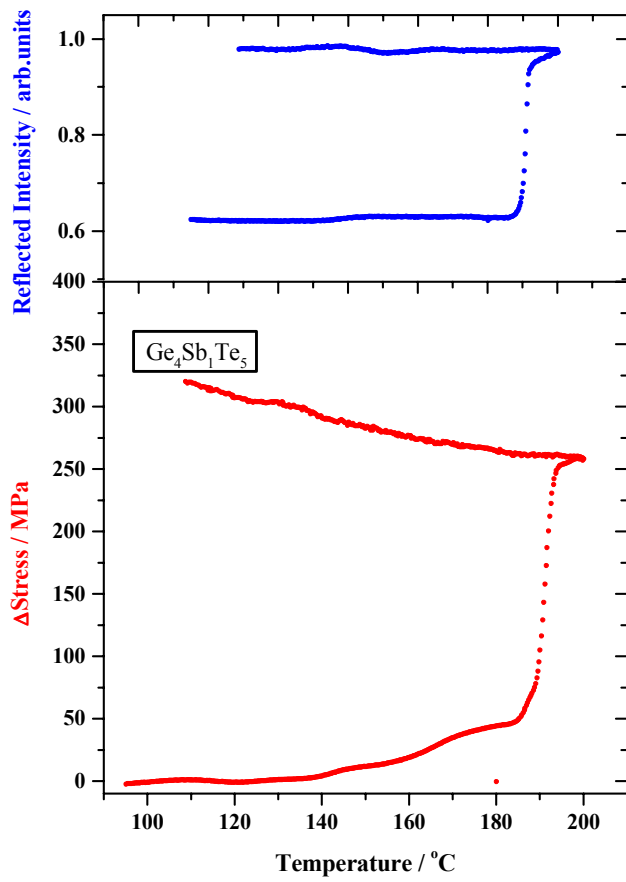


Figure 2(c)

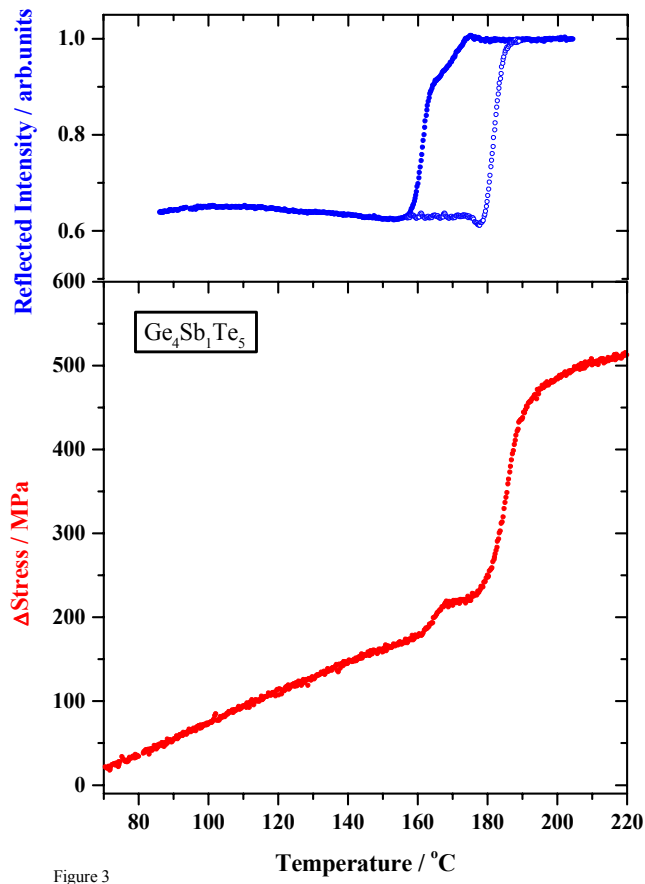


Figure 3