Mechanical stresses upon crystallization in phase change materials

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Crystallization processes in different Te alloys, employed in phase change materials for optical data storage, have been investigated by *in situ* mechanical stress measurements. Upon crystallization a considerable stress buildup 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 of stress relief phenomena comes from the temperature dependence of the stress in the crystalline and amorphous states. Ultrathin dielectric layers have a profound influence on the crystallization process as evidenced by simultaneous optical reflectance and mechanical stress measurements. This observation can be explained by heterogeneous nucleation of crystallites at the interface between the dielectric layer and the phase change film. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1415419]

In phase change recording the reversible transformation between an amorphous and a crystalline state is employed to write and erase information. The pronounced 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. This is one of the attractive features of this optical recording technology, which shows high potential for multimedia application. Nevertheless phase change recording also faces several challenges, in particular concerning the speed of the write and erase process and the durability (cyclability) of the media.[1,2] The limited cyclability could be a major concern if phase change media were to replace hard disk drives in demanding applications such as file servers, etc. The cyclability is affected by various properties of the phase change media, including the temperature profile in the layer stack,[3,4] the dielectric layers surrounding the phase change film,[5,6] and even its composition.[7,8]

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 $Ge_2Sb_2Te_5$, and 170 °C for $Ge_4Sb_1Te_5$. In all cases crystallization is accompanied by a considerable

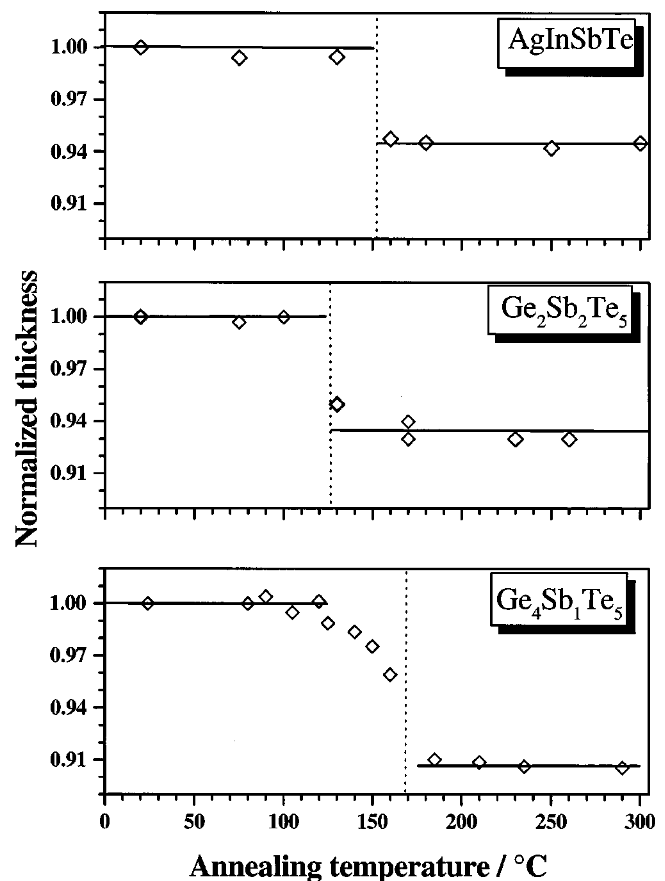

FIG. 1. Film thickness of AgInSbTe, $Ge_2Sb_2Te_5$, and $Ge_4Sb_1Te_5$ films as a function of increasing annealing temperature as measured by x-ray reflectometry. Crystallization, which leads to a sudden decrease in film thickness, is observed at 155 °C for AgInSbTe, 130 °C for $Ge_2Sb_2Te_5$, and 170 °C for $Ge_4Sb_1Te_5$. The more gradual thickness change upon annealing for $Ge_4Sb_1Te_5$ 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 $Ge_2Sb_2Te_5$, and a 9% thickness reduction for $Ge_4Sb_1Te_5$.

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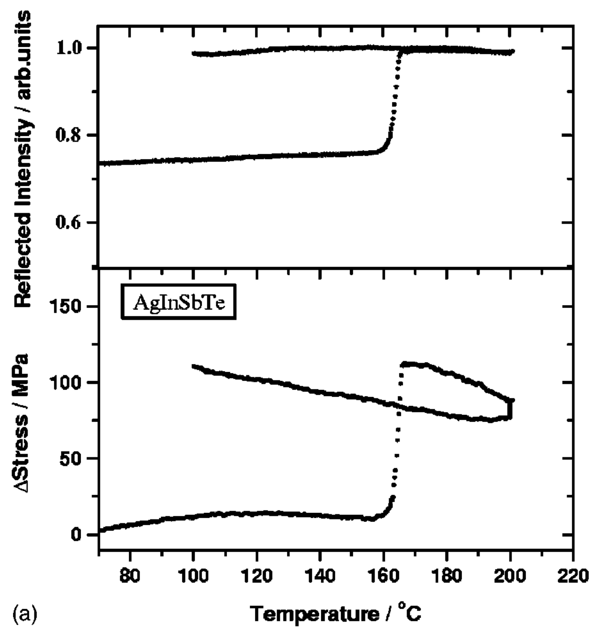

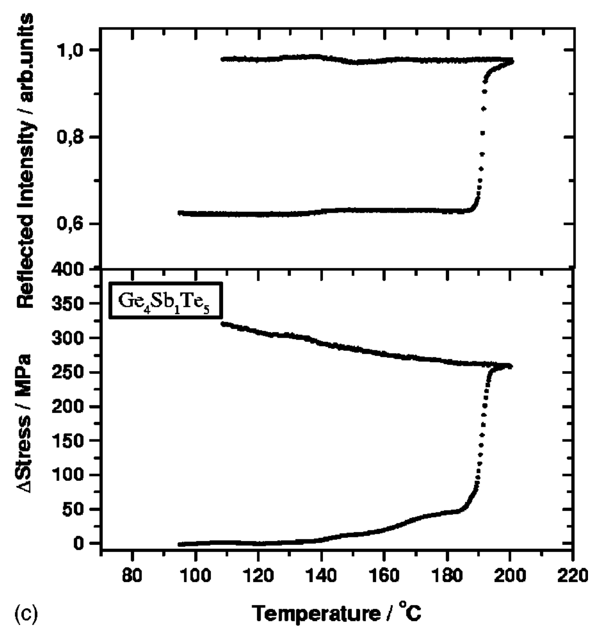

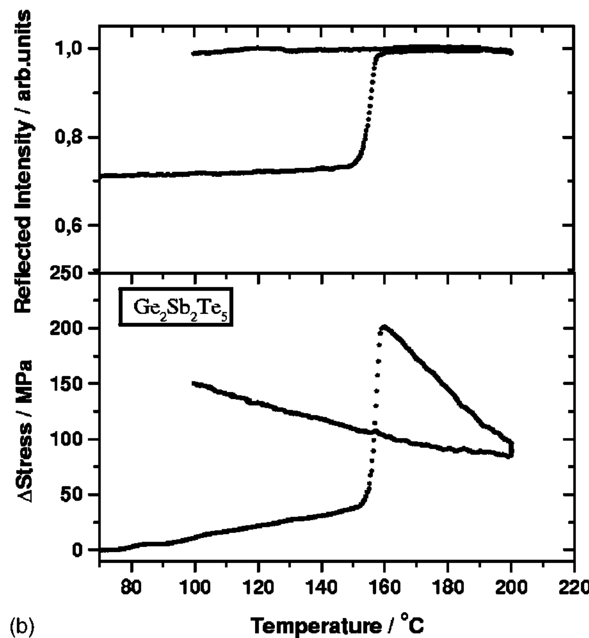

FIG. 2. Stress and reflected intensity from: (a) 85 nm AgInSbTe on a 150 μm glass substrate, (b) 85 nm $Ge_2Sb_2Te_5$ on a 200 μm Si wafer, and (c) 61 nm $Ge_4Sb_1Te_5$ on a 200 μm Si wafer. For all materials studied here the reflectance change upon crystallization is accompanied by an irreversible stress 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 min 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.

reduction in film thickness. The smallest thickness decrease of 5.5% is observed for AgInSbTe, while $Ge_2Sb_2Te_5$ shows a 6.5% thickness decrease upon crystallization. $Ge_4Sb_1Te_5$ 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.[9] We have also observed such stress induced effects in atomic force microscopy (AFM) images of crystalline bits, which were produced by a pulse of a focused laser.[10] 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[11] 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[12]

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

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

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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. $\varepsilon_{zz\ \mathrm{total}}$ describes the total change in film thickness upon crystallization, while $\Delta\sigma_{\mathrm{elast}}$ is the expected stress change upon crystallization assuming elastic behavior. The observed stress change is denoted as $\Delta\sigma_{\mathrm{exp}}$.

	$\alpha(10^{-5}/\mathrm{K})$	M_f (GPa)	$\varepsilon_{zz\ \mathrm{total}}$ (%)	$\Delta\sigma_{\mathrm{elast}}$ (GPa)	$\Delta\sigma_{\mathrm{exp}}$ (GPa)
AgInSbTe	1.50 ± 0.04	53 ± 1	$-(5.5\pm0.2)$	1.5	0.105
$Ge_2Sb_2Te_5$	1.81 ± 0.06	50 ± 2	$-(6.5\pm0.2)$	1.7	0.165
$Ge_4Sb_1Te_5$	1.99 ± 0.18	47 ± 4	$-(9.0\pm0.3)$	2.3	0.215

film, respectively, and $1/R_0$ and $1/R$ 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. Figure 2(a) displays the reflectance (top portion) and the mechanical stress (lower portion) for a 150 μm 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 buildup 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 Table I. While the coefficient of thermal expansion for the crystalline phase varies between 1.50×10^{-5}/K for AgInSbTe, 1.81×10^{-5}/K for $Ge_2Sb_2Te_5$, and 1.99×10^{-5}/K for $Ge_4Sb_1Te_5$, respectively, the biaxial elastic modulus for the crystalline phase ranges from 53 GPa for AgInSbTe to 50 GPa for $Ge_2Sb_2Te_5$ and 47 GPa for $Ge_4Sb_1Te_5$. 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[13] the stress change is $\Delta\sigma = -M_f(1-\nu)_f/(1+\nu_f)\varepsilon_{zz_{\mathrm{total}}}$, where ν_f is the Poisson ratio and $\varepsilon_{zz_{\mathrm{total}}}$ the total expansion in the 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 v_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 $Ge_2Sb_2Te_5$, and 2.3 GPa for $Ge_4Sb_1Te_5$. The measured stress change is much smaller, however, and corresponds to 105 MPa for AgInSbTe, 165 MPa for $Ge_2Sb_2Te_5$, and 215 MPa for $Ge_4Sb_1Te_5$. Hence, only a fraction of approximately 9% of the calculated stress change (assuming elastic behavior) 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 Fig. 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 100 s 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 buildup and the resulting viscous flow of the material upon crystallization.

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.

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