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Supporting information for article:

Crystallization of Ge₂Sb₂Te₅ and nitrogen-doped Ge₂Sb₂Te₅ phase-change-materials thin films studied by in situ combined X-ray scattering techniques

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APPENDIX A

Stress, elasticity and thermal dilatation considerations

From the plot of figure 7 and equation 1, the stress free d-spacings ($d_{\text{stress free}}$) d_0 and the film stress states (σ_{film}) are calculated. The obtained values are listed in table 4 for the three samples

# name	σ_{film} (MPa)	$d_{\text{Stressfree}}^{T_{\text{amb}}}$: (200) stress free d-spacing (Å) at T_{amb}
GST	123	3.0164
N : GST	99	3.0439
N+ : GST	75	3.0540

Table 4 Residual biaxial stress σ_{film} and (200) stress free d-spacing (by using $E_{\text{film}} = 35$ GPa and $\nu_{\text{poisson}} = 0.23$) measured at ambient temperature in thin film samples after the isothermal annealing T_{iso} for GST, N:GST and N+:GST layers.

Moreover, the Coefficient of Thermal Expansion (CTE) of GST film can also be deduced from XRD measurements and is estimated to be $\text{CTE}_{\text{film}} \approx 1.3 \cdot 10^{-5} \text{ K}^{-1}$ (the results are not shown here, but are in agreement with the work of Leervad et al., 2001). It will be assumed hereafter that N incorporation has a negligible effect on this CTE value. The CTE difference between PCM layers and Si substrate ($\text{CTE}_{\text{silicon substrate}} \approx 2.6 \cdot 10^{-6} \text{ K}^{-1}$ webelements.com) has an influence on the stress state of the sample. In an elastic hypothesis, the thermal biaxial stress ($\Delta\sigma_{\text{th}}$) induced in the GST film due to CTE difference with its Si substrate, is given by equation 2. Then, the thermal stress correction ($\Delta\sigma_{\text{th}}$) can be calculated at each temperature of interest, i.e. at the isothermal annealing temperature T_{iso} . An elastic behavior of the sample during cooling is assumed.

$$\Delta\sigma_{\text{th}} = \frac{E_{\text{film}}}{1-\nu_{\text{film}}} (\text{CTE}_{\text{film}} - \text{CTE}_{\text{substrate}}) (T_{\text{iso}} - T_{\text{amb}}) \quad (2)$$

As a result, the intrinsic stress (σ_{intr}) in the PCM film, generated only and intrinsically by the phase change (crystallization), can thus be calculated by using equation 3 and results for the 3 GST films are reported in table 5.

$$\Delta\sigma_{th} = \sigma_{film} - \sigma_{intr} \quad (3)$$

# name	$\Delta\sigma_{th}$ between T_{iso} and T_{amb} (MPa)	σ_{intr} (MPa)
GST	33	90
N : GST	52	47
N+ : GST	66	9

Table 5. Thermal biaxial stress variation $\Delta\sigma_{th}$ between isothermal annealing temperature (T_{iso}) and ambient temperature (T_{amb}) for the 3 GST films. From eq. 3, one can deduce σ_{intr} the biaxial intrinsic stress build-up only induced by crystallization for GST, N:GST and N+:GST films.

Analogously, thermal expansion issue has to be also considered here since it may obviously impact the d-spacings values measured and discussed above. Firstly, the stress free (200) d-spacings ($d_{stressfree}^{T_{iso}}$) at T_{iso} can be calculated by using equation 4 and $d_{stressfree}^{T_{amb}}$ measurements done *ex-situ* at T_{amb} (see Table 6):

$$d_{stressfree}^{T_{iso}} = d_{stressfree}^{T_{amb}} (1 + CTE_{film}(T_{iso} - T_{amb})) \quad (4)$$

Secondly, by means of combination of equations 1, 3 and 4 and previous measurements, the \perp (200) d-spacings at T_{iso} $d_{\perp}^{T_{iso}}$ can be calculated by using equation 5 and results are listed in Table 6.

$$d_{\perp}^{T_{iso}} = d_{\perp}^{T_{amb}} + d_{stressfree}^{T_{amb}} \left(CTE_{film}(T_{iso} - T_{amb}) \left(1 - \frac{2\nu_{film}}{E_{film}} \sigma_{intr} \right) + \frac{2\nu_{film}}{E_{film}} \Delta\sigma_{th} \right) \quad (5)$$

Isotropic dilatation and isotropic elastic properties are assumed. We emphasize that such assumptions are justified because PCM films are not textured.

# name	$d_{stressfree}^{T_{iso}}$: Stress free (200) d-spacing (Å) at T_{iso}	$d_{\perp}^{T_{iso}}$: \perp (200) d-spacing (Å) at T_{iso}
GST	3.0192	3.0156
N:GST	3.0483	3.0437
N+:GST	3.0595	3.0591

Table 6. Stress free (200) d-spacing and \perp (200) d-spacing at isothermal annealing temperature (T_{iso}) for GST, N:GST and N+:GST and calculated by using equation 4 and 5. The value are plotted on figure 6.

The \perp (200) d-spacings at T_{iso} calculated above are plotted as dash lines in figure 6 for the three samples. Based on the hypothesis of tri-axial stress ($\sigma_{11} = \sigma_{22} = \sigma_{\parallel}$ and $\sigma_{33} = \sigma_{\perp} \neq 0$) should be revisited and the strain ε^{Ψ} is expressed by equation 6. Then, the intrinsic stress σ_{intr} can be calculated from equation 7.

$$\varepsilon^{\Psi} = \frac{1+\nu_{film}}{E_{film}} (\sigma_{\parallel} - \sigma_{\perp}) \sin^2 \psi + \frac{\sigma_{\perp}}{E_{film}} - \frac{2\nu_{film}}{E_{film}} \sigma_{\parallel} \quad (6)$$

$$\sigma_{intr} = \sigma_{\parallel} - \sigma_{\perp} \quad (7)$$

APPENDIX B

Density calculation from XRR measurements

In-situ X-ray Reflectivity characterization is a powerful tool in order to probe the dynamic of volume shrinking during the isothermal annealing. The analytical simulations of XRR curves using the Parratt formalism give thickness values that are similar to values deduced from the Fourier transform of the Kiessig fringes. Since film density change are expected to be very small, the densities are extracted from critical angles determination. According to Snell's law

density and critical angle are directly proportional. Thus, densities can be calculated by using equation 8:

$$\rho = \frac{A\pi\omega_c^2}{10^6 r_e \lambda^2 N_A (Z+f')} \quad (8)$$

where ω_c is the critical angle, A and Z the atomic mass and atomic number, λ the X-ray wavelength, N_A the Avogadro's number, r_e the electron radius and f' the real anomalous dispersion. For instance in the case of $\text{Ge}_2\text{Sb}_2\text{Te}_5$, $\rho \approx 190228. \omega_c^2$. The thermal dilatation of the film has a negligible effect on the densities values deduced here (i.e. order of magnitude below $10^{-3} \text{ g.cm}^{-3}$).

APPENDIX C

Density calculations from XRD measurements

The following hypothesis are made: Firstly, we assume that all Ge, Sb and Te atoms are located in the crystalline phase after annealing. Secondly, we assume there are no atoms in interstitial sites, substitutional sites and no vacancies. This implies also that nitrogen incorporated is located at grain boundaries and a low Ge diffusion at grain boundaries (GeN_x). By means of compositions measured by PIXE, NRA and RBS, the density of the crystalline phase is calculated by using equation 9:

$$\rho^{XRD} = \frac{\sum_i^{Ge,Sb,Te} \{ (4 \eta_{\%}^i A^i \sum_i^{Ge,Sb,Te} \text{SOF}^i) \}}{100 N_A (2 d_{200})^3} \quad (9)$$

Where SOF^i is the site occupancy factor of element i (0.4 for Ge or Sb and 1 for Te), $\eta_{\%}^i$ is the atomic percent of element i in the film (table 1), N_A the Avogadro's number, A^i the mass number of the element i, and d_{200} the d-spacing measured at ambient temperature (table 2). Some attempts have been tried to insert up to 10% of Ge vacancies in our structure and this results in a density decrease lower than 0.1 g.cm^{-3} which is considered to be negligible in our work. Ge vacancies are sometimes observed in GST material (Kolobov et al., 2012). These rough

approximations enable the determination of a maximum density value, by considering our samples as nearly perfect crystals, in opposition to the minimum density value (measured by XRR), by considering our samples as a mixture of crystallites, grains boundaries, residual amorphous aggregates, voids...