

Real structure and in-situ transformation of Phase Change Materials

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The function of Ge-Sb-Te Phase Change Materials (PCMs) is based on a reversible switching between amorphous and crystalline state, cf. their use for optical information storage [1, 2], like rewritable DVDs and the BD system. For gaining a deeper understanding of the structural changes interrelated with information transfer, in-situ crystallization experiments inside a TEM were performed on thin films of $\text{Ge}_2\text{Sb}_2\text{Te}_5$, GeSb_2Te_4 and $\text{Ge}_2\text{Sb}_2\text{Te}_4$. The PCM films were deposited on Si wafers and glass substrates by dc magnetron sputtering from stoichiometric compound targets. The crystallization starts when increasing the dose, e.g. by adjusting the emission parameters and changing the condenser aperture. Comparisons of in-situ crystallized and ex-situ annealed crystalline films proof that analogous real structures were formed. Based on this finding we suppose that the in-situ crystallization is caused by beam heating.

In all cases the as deposited films were fully amorphous, cf. Fig. 1a for the showcase of GeSb_2Te_4 . Furthermore EDX nanoprobe analyses confirm the chemical homogeneity by the low variances for the single point measurements which were performed inside different areas. The initial step of crystallization is analogous for all materials, namely the formation of seeds (see asterisks in Fig. 1b, bottom) with cubic structure embedded inside an amorphous matrix. Consequently, the diffuse intensity recorded after initial crystallization (Fig. 1a, top vs. Fig. 1b, top) concentrates into a characteristic pattern of Bragg intensities expected for rotationally disordered grains with cubic structure. More extended times of irradiation just slightly increase the sizes of the cubic seeds. However, finally a partial ordering of cations and vacancies inside the (111)cub-layers of the seeds force a reduction of the average symmetry from cubic to trigonal as indicated by the lines with bright spots in HRTEM micrographs, see arrows in Fig. 1c.

Depending on the chemical composition distinct mechanisms for the final crystallization steps and specific microstructures were obtained. In case of $\text{Ge}_2\text{Sb}_2\text{Te}_4$ the characteristic grain-structure of the PCMs disappears and like for the ex-situ annealed films extended crystalline areas with well-separated nanolamellae are formed. Contrary to all other analyzed materials, this transformation proceeds even outside the directly irradiated area and is interconnected with strong mechanical stress. The SAED patterns of distinct zone axis orientations clearly reflect the single-grain nature of the films, and with a restriction to main

structure reflections the patterns could be approximated assuming a rhombohedrally distorted simple NaCl-type structure model ($a \sim 6 \text{ \AA}$). The perfection of the lamellar nanostructure is indicated by specific scattering phenomena, like the satellite reflections.

The distinct microstructures of the stable and metastable PCMs are accompanied by remarkably differing thermoelectric properties [3]. This finding initiates an extended study with the aim of characterizing the influence of chemical alloying, defects and the microstructures on physical properties.

1. M. Wuttig, D. Lüsebrink, D. Wamwangi, W. Welnic, M. Gilleßen, R. Dronskowski, *Nature Mater.* **6** (2007) 122.
2. A. V. Kolobov, P. Fons, A. I. Frenkel, A. L. Ankudinov, J. Tominaga, T. Uruga, *Nature Mater.* **3** (2004) 703.
3. V. Giraud, J. Cluzel, V. Soussa, A. Jacquot, A. Dauscher, B. Lenoir, H. Scherrer, S. Romer, *J. Appl. Phys.* **97** (2005) 97.
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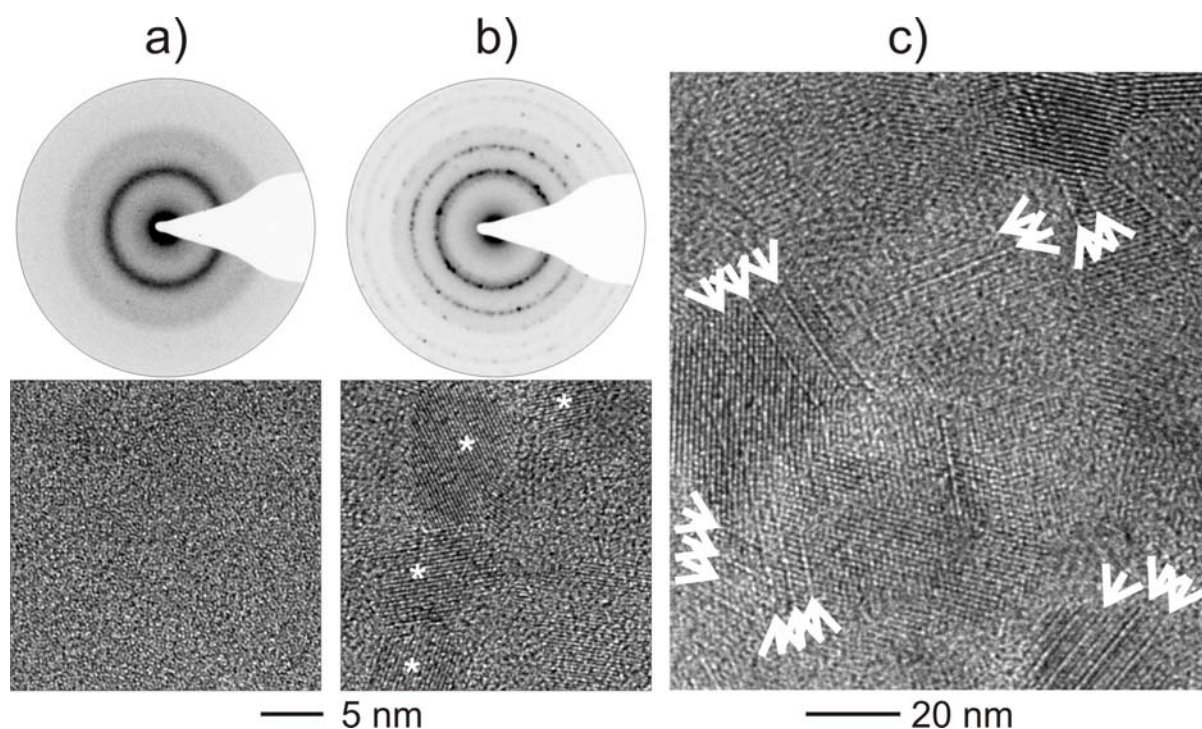


Figure 1. SAED patterns and HRTEM micrographs for as deposited GeSb₂Te₄ (a, amorphous) and after initial crystallization (b, the asterisks mark seeds with cubic average structure). c) Final stage of the real structure of GeSb₂Te₄, see text.