# Thin Films and Coatings

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## *In situ* and *ex situ* transmission electron study of the crystallization kinetics of $Ag_4In_3Sb_{67}Te_{26}$

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In optical data storage phase-change materials have been successfully established [1] and are promising candidates for non volatile electronic memory applications [2]. The crystallization kinetics is mainly defined by the writing speed and the stability of the phase-change data storage. Therefore sophisticated knowledge of the crystallization kinetics of phase-change materials is needed. Recent topics are the growth velocity of fast growth materials like $Ag_4In_3Sb_{67}Te_{26}$ (AIST) and the differences between as-deposited and melt-quenched AIST.

In the present work, the crystallization kinetics of AIST is investigated by *in situ* and *ex situ* heating. The *in situ* heating experiment is carried out with a Phillips PW 6592 *in situ* heating holder inside of a FEI Tecnai F20 transmission electron microscope (TEM). The *ex situ* heating is carried out inside of the heating furnace of a differential scanning calorimeter (DSC) for a high precision temperature control of ± 0.1 K.

The 30 nm thick amorphous AIST layer is embedded in a supporting multilayer stack on a 500 µm thick silicon substrate (“Figure 1.”). The 100 nm thick ZnS-$SiO_2$ capping layer on top of the AIST layer prevents oxidation. The 10 nm thick ZnS-$SiO_2$ layer below the AIST layer decreases together with the capping layer the necessary power to melt the AIST layer by laser irradiation. The 50 nm thick $Si_3N_4$ layer is an etch stop needed to prepare the TEM samples. The silicon substrate delivers sufficient heat dissipation for melt quenching. The AIST is either investigated in the as-deposited or in the melt-quenched state. Melt quenched amorphous marks (bits) are produced by laser irradiation of crystallized AIST. The AIST is crystallized beforehand in a furnace. To investigate the samples in a TEM the silicon substrate is removed by dimple grinding and etching with potassium hydroxide.

The *in situ* heating experiment is carried out with the AIST samples prepared by melt quenching. First of all the sample is heated from room temperature to 343 K and then heated to 383 K after the thermal drift has faded. The bits crystallize by inward growth from the crystalline rim towards the centre of the bit. The crystalline rim grows homogeneously into the bit. At 383 K the crystallization of a complete bit takes around 30 minutes after the heating starts. There is no nucleation observed inside the bit. This shows clearly the growth dominated crystallization behaviour of AIST. Bending contours created during crystallization follow approximately the crystal growth direction. The crystallized area shows little difference in morphology to its surrounding crystalline matrix (“Figure 2.”).

In the *ex situ* heating experiment the growth velocity of as-deposited AIST is quantitatively measured. The samples are annealed in the temperature range of 413.15 K-428.15 K. As soon as measurable grains have crystallized the samples are switched between TEM and further heating in the DSC. The grain size is measured in TEM brightfield images after each heating step. The morphology of the growing grains in the as-deposited layer is the same as the morphology of the area from the melt-quenched bit after crystallization. Bending contours in the growing grains are clearly visible. The average growth velocities are calculated from the measurements of several round grains in a few samples for every temperature. The grains are growing mainly homogenously round. The size of the diameter of the grains increases linear over time at a given temperature. The growth velocity increases exponential with increasing temperature. The *ex situ* heating will be also performed with melt-quenched AIST and compared to the as-deposited state.

1. E. Meinders, A. Mijiritskii, L. Pieterson and M. Wuttig in “Optical Data Storage: Phase-change Media and Recording”, ed. F. Toolenaar, (Springer, Netherlands) (2006), p. 18.
2. M. Wuttig and N. Yamada, Nature Materials 6, (2007), p. 824.
3. J. Heber, D. Schlom, Y. Tokura und R. Waser in “Frontiers in Electronic Materials”, ed. M. Wuttig, (Wiley-VCH, Deutschland) (2012), p. 175.
4. We kindly acknowledge the funding from the DFG in the framework of the SFB 917 “Nanoswitches”.

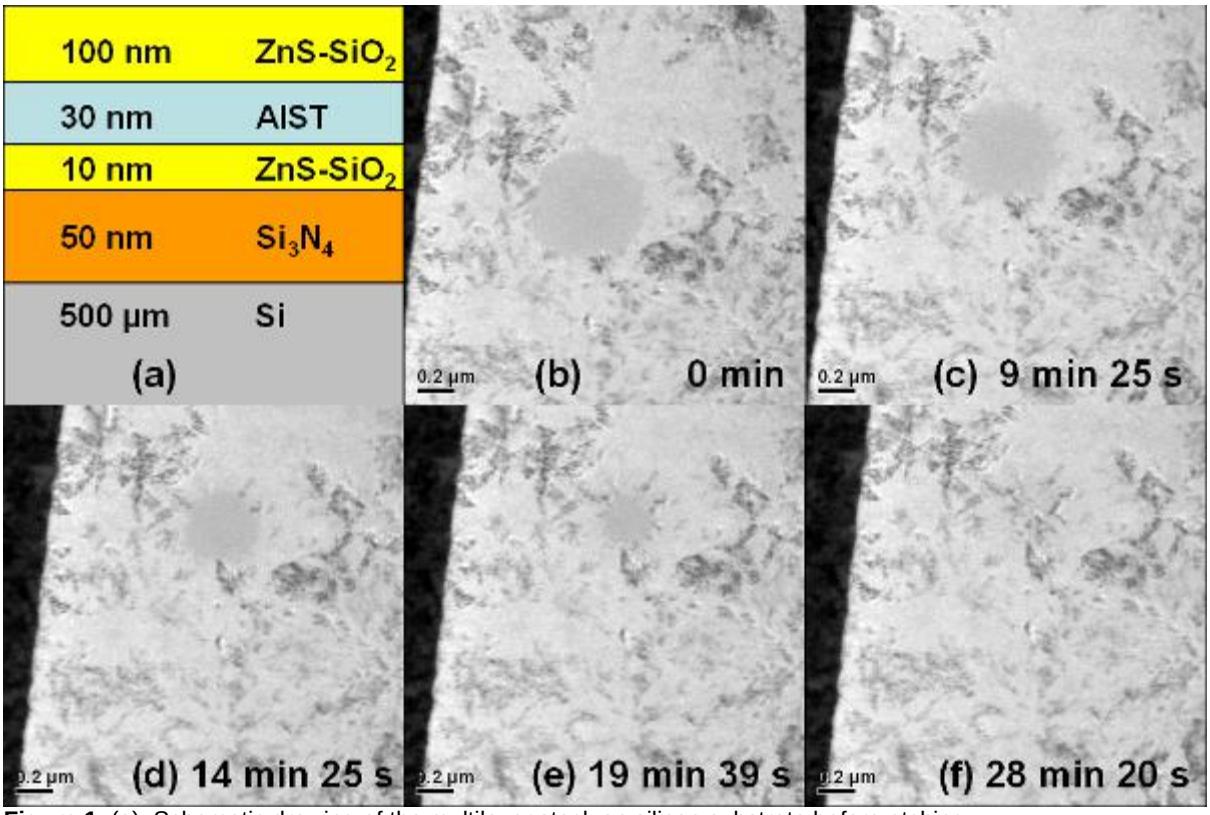


**Figure 1.** (a). Schematic drawing of the multilayer stack on silicon substrate before etching.
(b)-(f). Transmission electron microscope brightfield images of an amorphous melt quenched region within a crystalline $Ag_4In_3Sb_{67}Te_{26}$ layer heated *in situ* at 383 K. The displayed time is related to the start of heating [3].

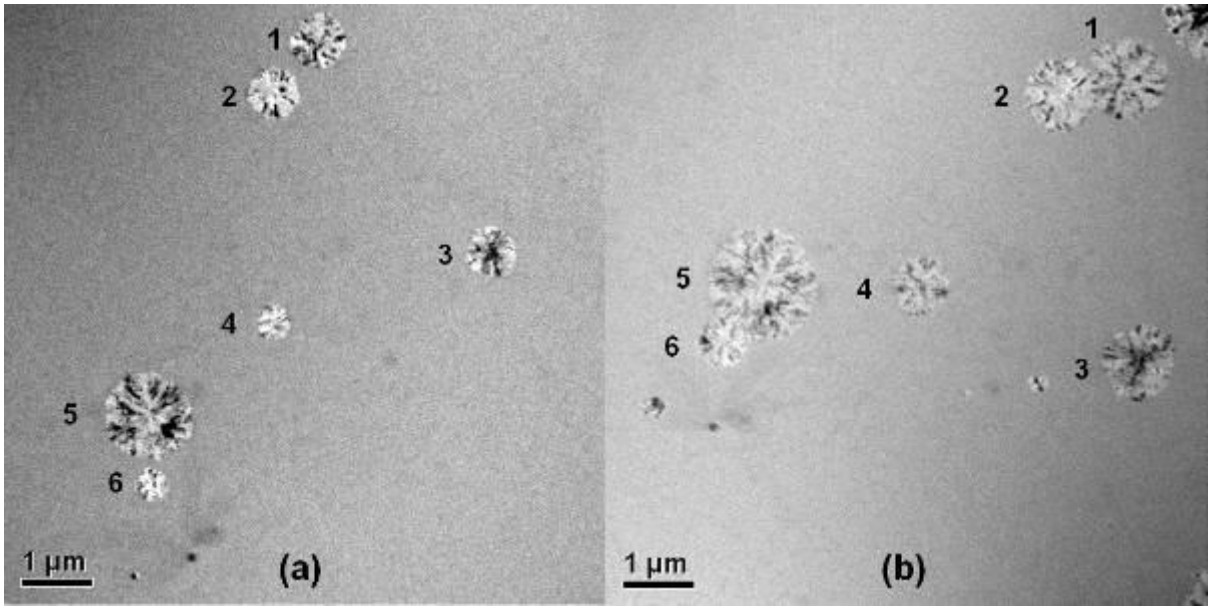


**Figure 2.** (a). Transmission electron microscope brightfield image of crystalline grains in a amorphous $Ag_4In_3Sb_{67}Te_{26}$ layer after 90 min *ex situ* heating in a furnace at 418.15 K.
(b). The grains from image (a) after 10 min additional heating (100 min in total) at 418.15 K.