

Real Structure and Structural Changes of Functional Tellurides

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Nowadays, functional tellurides are widely used as bulk- and nanomaterials for thermoelectric power generators and phase-change based applications, e.g. optical data storage. The function and performance of the materials strongly depend on their unique nanostructural properties and their structural evolution upon operation. Both features can be fully characterized in-situ, ex-situ and on a broad range of length scales by combining diverse characterization techniques with transmission electron microscopy. Consequently, essential information about real-structure property relations and fatigue mechanisms can be determined enabling first steps to a knowledge-based tailoring of the materials.

Crystalline phase change materials with general formula $(\text{GeTe})_a(\text{Sb}_2\text{Te}_3)_b$, are based on a rocksalt-type structure. The cation sites of the parent structure are occupied by Ge and Sb atoms as well as a molar fraction of $c = b - a$ structural vacancies per formula unit. Distinct arrangements of the structural vacancies are observed in the course of thermal operation. Starting with amorphous thin films in-situ observations prove a two-step mechanism for the crystallization of most of the GeTe-rich ($a > b$) phases [1]. Firstly crystalline but metastable nanoparticles with random distribution of structural vacancies are formed; secondly these vacancies are combined to layered aggregates, the so called vacancy layers. The distances in-between the vacancy layers scales with the GeTe content (a). This crystalline state with trigonal average structure remains stable upon long-term annealing. In order to derive information about the intermediate state in-between random disorder and layered aggregation of structural vacancies we applied in-situ microscopy on chemically modified phase change materials. In case of Sn-doped thin films we firstly observed the evolution of diffuse scattering by means of in-situ heating experiments. Such indicator for pronounced short-range ordering of the structure is assumed to be interconnected with a correlated arrangement of the structural vacancies.

Telluride bulk- and thin-film materials were also regarded promising candidates for thermoelectric applications, particularly when introducing chemical and/or structural segregation (so called nanostructuring [2]) of the materials to reduce the thermal conductivity, and thus enhancing thermoelectric efficiency. However, nanostructuring as metastable feature of materials is frequently degrading in the course of thermoelectric application. Recently, we probed the thermoelectric efficiency and stability of doped phase change materials by introducing them into thermoelectric power generators [3]. Such optimized benchmarking of thermoelectric materials is not restricted to the determination of the intrinsically imprecise thermoelectric figure of merit (ZT value), and gives information about the microstructural and performance changes during thermal operation of the materials. Consequently, failure mechanisms can be determined and the resistance of the materials against functional and microstructural fatigue can be specified. In case of a low doping level of the phase change material the microstructure of the as-prepared material remains unchanged upon thermal cycling, consequently,

excellent and stable thermoelectric performance was obtained. For higher doping level we observed strain phenomena for the as-prepared state which are released by the formation of planar defects after thermal cycling. Consequently, the thermoelectric performance degrades significantly upon repeated thermal cycling.

In a second set of experiments, we analyzed the thermal stability of chemically segregated $(\text{Bi}_2\text{Te}_3)_a(\text{Sb}_2\text{Te}_3)_b$ superlattices [4,5] which were firstly prepared by molecular beam epitaxy. Starting at $T = 200\text{ }^\circ\text{C}$, the superlattice structures are gradually transformed into the homogeneous alloy. In-situ microscopy proves that the interdiffusion preferably starts next to chemical defects of the superlattice while areas with low density of defects remain stable up to $300\text{ }^\circ\text{C}$. These observations suggest that the structural integrity of the superlattices critically depends on the defect density of the material as further supported by recent in situ- and ex situ observations.

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