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Structural properties of thermoelectric $CoSb_3$ skutterudite thin films prepared by molecular beam deposition

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ABSTRACT

The research field of thermoelectricity was renewed by the progress made in nanostructuring approaches and by the investigation of new material groups as skutterudites, whose most promising representative is $CoSb_3$. In this work Co–Sb thin films with a thickness of 30 nm were deposited by molecular beam deposition at different substrate temperatures as well as on non-heated substrates followed by a post-annealing step. An extended investigation of the phase formation in dependence of deposition method and parameters, film composition, and post-treatment is given. The presented results provide different routes to achieve high quality single phase films. It was also demonstrated that the grain size of the $CoSb_3$ thin films is very sensitive to the used deposition method and especially on the substrate temperature during deposition. A controllable grain size by changing the deposition parameters could be a key feature for the optimization of the thermoelectric properties, since especially the thermal conductivity should strongly depend on the grain size due to enhanced grain boundary scattering of phonons.

1. Introduction

The field of thermoelectric power generation becomes more and more important, since new energy sources have to be found and existing ones have to be used more efficiently. For commercial application the use of thermoelectric materials was not competitive for decades, since their efficiency was very low. A good thermoelectric material has to have a large Seebeck coefficient S, a high electric conductivity σ, and a low thermal conductivity κ, which can be summarized in the dimensionless figure of merit: $ZT = S^2\sigma T/\kappa$. Since all these coefficients are coupled to each other, an enhancement of ZT is challenging.

The research field was renewed by the progress made in thin film and nanostructuring technologies. For instance, thin film techniques deliver several methods to decouple the coefficients and to enhance ZT [1–9]. Additionally new material groups like skutterudites with special crystal structure were found [10,11]. Guest ions can be incorporated into the voids (2a sites) of the crystal structure yielding a lower thermal conductivity while maintaining the other coefficients constant. The underlying idea is called phonon glass-electron crystal (PGEC) approach and was first introduced by Slack [12]. The most promising skutterudite investigated at the moment is $CoSb_3$. The synthesis of single-phase $CoSb_3$ thin films is a challenge as the phase diagram shown in Fig. 1 reveals no homogeneity area for the single $CoSb_3$ skutterudite phase [13]. The phase should be only observed for an accurate stoichiometry with 75 at.% Sb. For lower Sb content $CoSb_2$ is additionally formed, for higher Sb content the pure Sb phase will be supplementary obtained.

In literature several publications for skutterudite thin films prepared via sputtering [7,14–16], pulsed laser deposition (PLD) [17–20] or modulated elemental reactant method (MERM) [21–24] can be found, but all of them describe films thicker than 70 nm, which is in a range, where the benefits due to nanosize effects are limited. Many difficulties are reported in these works for achieving single-phase films, especially for film deposition on heated substrates. Caylor et al. [18] optimized the parameters for PLD and could achieve single-phase films for a narrow range of substrate temperatures during deposition. By an excess of Sb in the targets, this range can be shifted to higher temperatures. Colceag et al. [25] were not successful to prepare single-phase skutterudite films by PLD, but in their work a lower substrate temperature around 200 °C leads to the skutterudite phase as major phase. Suzuki [26] did not find a systematic dependency of the

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phase formation on the laser fluence, substrate temperature or Sb content in films prepared by PLD. Nevertheless, he was able to synthesize single-phase films at substrate temperatures below 250 °C. For very complex alloy targets ($Ce_{0.26}Co_{3.7}Ni_{0.26}Ge_{0.79}Sb_{11.21}$), the formation of diantimondides was reported for films prepared by PLD [19].

A more systematic investigation of the influence of the composition on the phase formation was performed for MERM deposited films (elements deposited layer-by-layer at room temperature followed by post-annealing), where the composition was varied between 68 at.% and 81 at.% of Sb. Here the formation of single-phase skutterudites was found for a Sb content between 74 at.% and 78 at.% [21]. For sputter deposited films on non-heated substrates, the additional formation of the Sb phase was reported [16,27].

To understand and overcome the described preparation problems, this work provides an extended investigation of the phase formation in dependence of deposition method and parameters, film composition, and heat treatment. Co–Sb thin films with a thickness of 30 nm were deposited via molecular beam deposition at different substrate temperatures as well as on non-heated substrates followed by a post-annealing step. For a comparison with other deposition methods such as sputtering, where a larger amount of energy is introduced, the influence of the chosen deposition rates was investigated.

2. Experimental methods

$CoSb_y$ films with a thickness of 30 nm were codeposited in an ultra high vacuum (UHV) chamber by molecular beam deposition with a base pressure between $5 \cdot 10^{-11}$ mbar and $5 \cdot 10^{-10}$ mbar. Thermally oxidized silicon (SiO_2(100 nm)/Si(100)) was used as substrate (4″ wafer or pieces). Since the SiO_2 is amorphous, the films were not grown epitaxially. The substrates were first introduced to a load lock and baked at 200 °C to remove water contamination. The deposition chamber is equipped with an electron beam evaporator for the evaporation of Co and an effusion cell for Sb. The flux of Co can be controlled instantaneously by an optical detector (via electron induced emission spectroscopy, EIES), which was calibrated by depositing a Co film with a specific nominal thickness. The real thickness and the corresponding tooling factor were afterwards determined by Rutherford backscattering spectroscopy (RBS). The deposition rate of Sb was controlled by the temperature of the effusion cell. For calibration, three Sb films were deposited at different temperatures using a deposition time of 10 min. The thicknesses of these films were also determined by RBS allowing the calculation of the corresponding deposition rates, which gives an exponential dependence on the effusion cell temperature.

The chosen nominal film composition of the codeposited Co–Sb films can be controlled by adjusting the individual deposition rates with respect to these calibrations. The nominal Sb deposition rate ϕ_{Sb} was 0.3 Å/s and the Co deposition rate ϕ_{Co} was adjusted between 0.047 Å/s and 0.020 Å/s to achieve the desired nominal composition Co_xSb_y by using

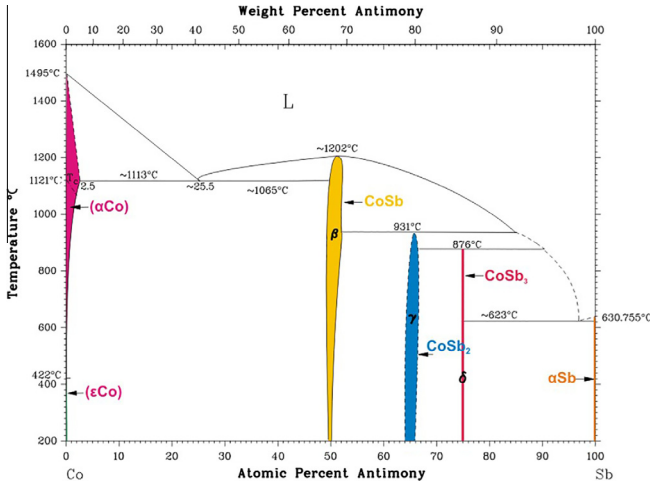

Fig. 1. Co–Sb phase diagram, where the nomenclature of the phases follows Massalski et al. [13].

$$\phi_T = \phi_{Sb} \frac{\rho_{Sb} M_{Co}}{\rho_{Co} M_{Sb}} \frac{x}{y},$$

where ρ_i and M_i are the mass densities and the atomic masses of the different elements, respectively. The film thickness was adjusted by the deposition time. To ensure homogeneous films, the sample holder was rotating during the deposition. Furthermore, a chamber wall cooling system prevented the film from contamination due to warmed-up side walls. For deposition at elevated substrate temperatures, the sample holder allowed the possibility to heat the substrate from the backside up to 1000 °C.

Additionally, the chamber was used for post-annealing of the film samples under UHV conditions. The films were therefore deposited on wafers and afterwards shortly exposed to air for breaking them into pieces. Different samples were mounted together, reintroduced and post-annealed for 1 h in UHV. The used heating rate to reach the final temperature was 10 K/min.

The composition and the thickness of as-deposited and annealed films were determined by RBS. He^+ ions were accelerated by a van de Graaff generator to 1.7 MeV and the used scatter angle was 170°. The backscattered ions were detected with a multichannel semiconducting detector. Usually the collected charge was 10 μC.

The phase formation in the films was investigated by X-ray diffraction (XRD) with a laboratory diffractometer, which was measuring in Bragg–Brentano geometry using Cu Kα radiation. A Ni filter on the primary side was used to decrease the Cu Kβ radiation, since no monochromator was implemented. On the secondary side a Soller collimator was installed. To increase the probed volume and to suppress the influence of the single crystalline substrates, usually a 2θ-scan (moving detector) with constant incident angle of 10° was performed. The contribution of the Cu $K_{\alpha 2}$ radiation was subsequently removed from the data by the Rachinger algorithm [28], thus the resulting XRD patterns correspond mainly to the Cu $K_{\alpha 1}$ radiation with a wavelength of 1.5406 Å. To identify peaks and phases, a literature data base [29] was used.

The surface morphology of the sample was imaged by atomic force microscopy (AFM). In this work an AFM of the type DI Dimension 3000 was used in the constant force tapping mode.

The as-deposited thin films were analyzed by differential scanning calorimetry (DSC) and characteristic crystallization temperatures were determined. The measurements were performed with a Netzsch DSC 200 system. First, a PMMA film was spin-coated on a Si(100) wafer. Afterwards the Co–Sb film was deposited at room temperature on top. By dissolving the PMMA layer in acetone, the deposited amorphous Co–Sb film could be lifted from the substrate and fished out. About 1.5 mg of the film material was put into an Al pan, while a second reference pan was left empty. Both pans were weighted before performing the measurements to correct mass differences between sample pan and reference pan. The heat procedure was performed in N_2 atmosphere with a heating rate of 10 K/min. The sample was heated two times and the DSC voltage was measured. The second curve was subtracted from the first one, to extract irreversible events.

To study the microstructure and the grain size, transmission electron microscopy (TEM) was used. Energy-filtered bright and dark – field images were acquired on cross section samples with a TEM Zeiss 912 Ω operated at 120 kV.

The grain size was further determined by electron backscatter diffraction (EBSD) in a FEI Nova NanoSEM 200 scanning electron microscope (SEM) using an incident angle of 70° and an electron energy of 15 keV.

3. Results and discussion

3.1. Structural properties of films deposited with different approaches

The fabrication of thin $CoSb_3$ skutterudite films with the correct stoichiometry and a mass fraction of secondary phases smaller than 5% is challenging. One reason is the non-existence of a homogeneity area in the Co–Sb phase diagram for the investigated skutterudite phase $CoSb_3$ (Fig. 1). Further difficulties occur due to the very high vapour pressure of Sb and the low sticking coefficient for the deposition of elemental Sb. For the deposition of elemental Sb on Si(100) substrates at moderate temperatures like 300 °C, there is for example only one monolayer of Sb stable [30]. As already mentioned, two different deposition approaches were tested: (i) codeposition of Co and Sb on non-heated substrates followed by post-annealing, and (ii) codeposition of Co and Sb at elevated substrate temperatures. Both approaches are illustrated in Fig. 2. The structural properties of the films prepared by applying these methods and the induced differences will be discussed in the following. Please note that *$CoSb_3$ films* is used as synonym for single-phase Co–Sb films exhibiting the skutterudite phase, while the Sb content of these films is not necessarily 75 at.%.