Determination of structural properties of thin thermoelectric \( \text{Fe}_{(1-x)}\text{Co}_x\text{Sb}_3 \) films using x-ray diffraction

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Since energy efficiency is becoming more and more important, the field of thermoelectricity is particularly in the focus of current research activities. Nanostructured materials [1, 2] as well as new material groups have recently been introduced [3, 4]. One of the promising materials for future applications is CoSb3 in its skutterudite phase.

CoSb3 is a p-type semiconductor with a band gap smaller than 0.4 eV. To optimise the electric conductivity and the Seebeck coefficient it is necessary to control the charge carrier concentration. For CoSb3 this could be achieved by a controlled substitution of Co atoms with Fe atoms and was already reported for bulk materials [5].

In this project we have investigated thin polycrystalline \( \text{Fe}_x\text{Co}_{1-x}\text{Sb}_3 \) films with \( x \) ranging from 0 to 1 on SiO2(100nm)/Si(100) substrates using x-ray diffraction at HASYLAB beamline G3 at a wavelength of 0.176 nm closely corresponding to CoK\( \alpha \) to avoid Co fluorescence radiation. The films were deposited at a substrate temperature of 200°C or at room temperature and post-annealed in UHV for 1h at 450°C.

A Rietveld refinement with the program FULLPROF [6] of the patterns of \( \text{Fe}_x\text{Co}_{1-x}\text{Sb}_3 \) in the range of \( 20° < 2\theta < 100° \) was done. Additionally, a series of stress measurements with the \( \sin^2(\psi) \) – method were performed for the \( \text{Fe}_x\text{Co}_{1-x}\text{Sb}_3 \) films to investigate the influence of stress on the lattice constant and the peak positions.

\( \text{Fe}_x\text{Co}_{1-x}\text{Sb}_3 \)

\( \text{Fe}_x\text{Co}_{1-x}\text{Sb}_3 \) were deposited by a co-deposition of Sb (effusion cell), Fe (effusion cell) and Co (e-gun) in a MBE chamber with base pressure of \( 10^{-10} \) mbar. Samples were deposited at a substrate temperature of 200°C and at RT with a post annealing step in UHV for 1h at 450°C. The Fe content \( x \) of the film was varied between 0 and 1.

The refinement (see fig 1(a)) of the measured patterns of the films deposited at 200°C reveal mainly the skutterudite phase and the Sb phase up to \( x = 0.15 \). Additionally CoSb2 could be found as minor

Figure 1: a) Refinement of the XRD-pattern of a \( \text{Fe}_x\text{Co}_{1-x}\text{Sb}_3 \) film deposited at 200°C. b) change of lattice constant with increasing Fe substitution \( x \). c) Effective charge carrier concentration in dependence of Fe content \( x \).
phase. This could be explained with the composition. RBS investigation show a Sb content of about 71 at. %, which is less than the desired composition of 75%. For higher x other additional phases (e.g. FeSb₂, CoSb₂) can be found and for x larger than 0.34 the skutterudite phase is not observed at all. The lattice constant was extracted with refinement and an increase with increasing Fe content was observed (see fig 1(b)). The observed change in lattice constant indicates a successful substitution, which was confirmed by the investigations of charge carrier concentration via hall measurements (see fig 1(c)). The material is p-type and an increase of charge carrier concentration p up to a Fe content of x = 0.35 could be found. Above this value p stays constant. The relaxation above x = 0.35 agrees with the amount of Fe (x=0.34), above which only impurity phases are formed.

The films deposited at room temperature and post-annealed to 450°C show better results. Two series were investigated, a Sb rich series (77.3 at.%) and Sb deficient series (72.5 at.%). Up to a Fe content of x = 0.5 only the skutterudite phase could be observed for both series. Even at x=0.6 the skutterudite phase is still the major phase and FeSb₂ as additional minor phase has formed. Above this concentration only FeSb₂ is formed. The lattice constant was extracted and the charge carrier concentration measured. The results agree with the characteristics found for the films deposited at 200°C. The lattice constant increases with increasing Fe content and the charge carrier concentration increases first and starts to get constant, when impurity phases occur (x=0.5).

Figure 2: a) XRD-pattern of FeₓCo₁₋ₓSb₃ films with different x. The films were deposited at room temperature and post-annealed at 450°C. b) Change of lattice constant with increasing Fe content x. c) Effective charge carrier concentration in dependence of Fe content x.

To make sure that the change of lattice constant and a change in the surface structure found by AFM is not caused by film stress due to the introduction of Fe atoms, sin² ψ measurements were performed. All films reveal a tensile stress of 0.3 GPa and no change with different x.

References