Investigation on the homogeneity of pulsed electrochemically deposited thermoelectric films with synchrotron μ-XRF, μ-XRD and μ-XANES

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Thermoelectric materials are capable to generate a voltage and current, when subjected to a gradient of temperature. A cost and time efficient production of thermoelectric units is the goal for future miniaturized thermoelectric generators based on thin films up to 200 µm. A comprehensive analysis of chemical and physical properties is a crucial part of the developments. One of the key parameters for the materials physical properties is the Seebeck coefficient \( S = \Delta U/\Delta T \), which is the generated voltage for a given temperature difference. To determine the origin of a variation of \( S \), which is found for thermoelectric materials, such as Bi\(_2\)Te\(_3\) an investigation on their stoichiometric and structural homogeneity is presented. Micro-X-ray fluorescence (μ-XRF) and micro X-ray diffraction analysis (μ-XRD) with 15 µm spot size is performed simultaneously with focused synchrotron X-ray radiation at 17.4 keV. Additionally micro-X-ray absorption near edge structure (μ-XANES) measurements are performed.

On a 5 to 15 µm thick Bi\(_2\)Te\(_3\) sample, which is deposited on a Si wafer on top of a 20 nm Au layer, \( S \) measurements are carried out spatially resolved. A sample is heated with a tip to 1.8 K above room temperature and the generated voltage is determined. A slight anisotropy is found as can be seen in figure 1A. μ-XRF and μ-XRD analyses showed homogeneous spatial elemental distribution, which was determined from the Te(L) and Bi(M) fluorescence intensities (1D), and structure [1]. Additionally figure 1 shows the μ-XRF map (1B) and the calculated sample thickness for a Bi\(_2\)Te\(_3\) (1C), which is determined from the Au fluorescence intensity.

The anisotropy of \( S \) matches the sample morphological profile. Thicker areas correlate with a higher absolute value of \( S \). When the \( S \) probe reaches the thinner parts of the deposited material,
the influence of the substrate (Au-layer) cannot longer be neglected. In contrast to $S$ the Te(L)/Bi(M) ratio was found homogeneous with $1.01 \pm 0.004 (0.4\%)$ over almost the whole deposit except the rim of the deposit, where a decrease of the ratio to $0.8 \pm 0.053 (6.6\%)$ for the outermost $50 \mu$m was found (Figure 1D).

On the Bi$_2$Te$_3$ deposit $\mu$-XANES experiments are performed at BiL3-Edge to monitor anisotropy of valence of the material. At five points as indicated in figure 2 XANES scans were performed. The results show that the thinner part in the middle is slightly more oxidized than the thicker rim of the sample.

Regarding these results we propose the origin of the variance of $S$ is found in the layered structure of the specimen of the material. We assume that in general all layers of the deposit including the $20 \text{ nm}$ Au contribute to $S$. The correlation of variances of $S$ with the thickness of the specimens found here indicates that the information depth of the Seebeck measurement is close to the thickness of our specimens. With a penetration depth of the applied heat between $5 \mu$m and $10 \mu$m the influence of the Au layer would only be detectable in the thinner parts of the sample.

Having shown the deposition homogeneity and having correlated the inhomogeneity of $S$ with the sample thickness variations the higher amount of oxidation in the thinner parts of the sample and the possible Au influence in the same region are two possible reasons for the inhomogeneity of $S$ since both factors may alter the materials properties severely.

The presented results were published previously [2] and explained in more detail there.

References