Influence of Electrolyte Concentration on Crystal Orientation and Seebeck Coefficient of Bi_2Te_3 Nanowires Arrays

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Bulk materials based on bismuth telluride (Bi_2Te_3) exhibit high thermoelectric efficiency at room temperature, being thus common constituents of thermoelectric devices operating at ambient conditions. The efficiency of a thermoelectric device is described by the figure of merit $ZT = S^2\sigma T/\lambda$, where S denotes the Seebeck coefficient, σ electrical, λ thermal conductivity, and T the absolute temperature. Theoretical calculations predicted an enhancement of the thermoelectric efficiency in low-dimensional Bi_2Te_3 structures, such as nanowires (NWs), due to finite- and quantum-size effects [1]. For NWs, the diameter clearly represents one of the crucial parameters for the enhancement of ZT. Bi_2Te_3 NWs had been synthesized by electrodeposition mainly in porous alumina membranes [2] displaying in most cases diameters above 50 nm. Recently, we have reported the electrodeposition of Bi_2Te_3 NWs with diameters as small as ~17 nm in the pores of etched ion-track membranes [3]. In addition, Bi_2Te_3 has a highly anisotropic crystal structure and the electrodeposition parameters can thus influence its crystal orientation and physical properties. Here we present systematic studies on the influence of electrolyte concentration on the crystallographic characteristics and Seebeck coefficient of 25-nm diameter Bi_2Te_3 NW arrays [4].

Polycarbonate foils (thickness 30 µm) were irradiated with ~GeV U ions at the UNILAC accelerator. The ion tracks were etched in 6M NaOH solution at 50 °C for 60 s to fabricate channels with diameter ~25 nm. Bi_2Te_3 NWs were electrodeposited in the channels using a thermostated three-electrode cell and a saturated calomel reference (SCE) electrode. The deposition was performed applying U = 0 mV vs. SCE at T = 4°C. The electrolytes were based on 1 M nitric acid, 5 mM tellurium powder and three different bismuth nitrate pentahydrate concentrations, namely 10 mM, 7.5 mM, and 3.5 mM Bi.

Bi_2Te_3 NW arrays synthesized with different electrolytes were characterized by x-ray diffraction (XRD) to study the preferential crystallographic orientation (Fig. 1). The XRD spectra display reflections assigned to the polycarbonate membrane, the Au cathode layer and the (101), (105), and (205) reflections from the Bi_2Te_3 NWs. The (101) reflection is small in all cases, while the NW array deposited with lowest Bi:Te ratio (green) displays the strongest, but still relatively weak, signal for (015) orientation. Finally, with increasing Bi:Te ratio in the electrolyte, an increase of the (205) reflection, i.e. (205) planes parallel to membrane surface, is noticeable.

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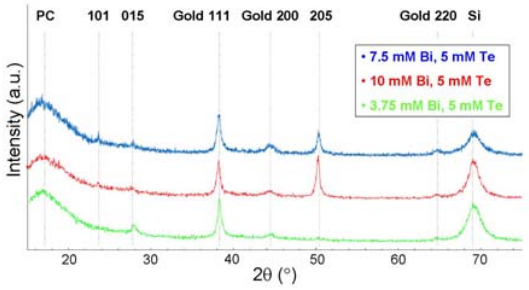

Fig. 1: XRD patterns of Bi_2Te_3 NW arrays deposited with electrolytes of Bi:Te ratio 3.75:5 (green), 7.5:5 (blue), and 10:5 (red) at T=4°C applying U=0 mV vs. SCE.

All samples show negative S values, indicating n-type behaviour, with a linear T dependence. The sample synthesized with the lowest Bi:Te electrolyte ratio exhibits highest S in the whole range, achieving S = -55.0 µV/K at 270°C, while NWs deposited with 7.5 mM Bi and 10 mM Bi, displayed S ~ -49.6 µV/K and -38.6 µV/K at 270 °C, respectively.

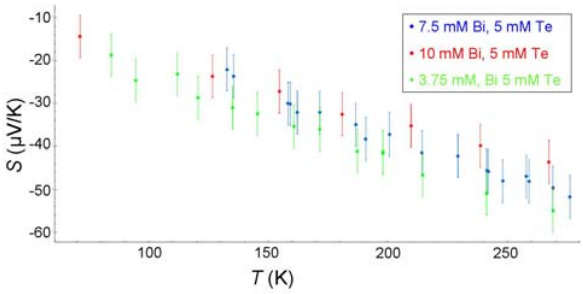

Fig. 2: Seebeck coefficient vs. temperature.

In conclusion, Bi_2Te_3 NWs arrays were electrodeposited in etched ion-track membranes using electrolytes with three different Bi:Te ratios. XRD measurements revealed an increasing (205) preferred crystallographic orientation for higher Bi concentrations in the electrolyte. Seebeck measurements indicate only a weak dependence of the S coefficient on the different Bi:Te ratio of the electrolyte.

[1] L.D. Hicks and M.S. Dresselhaus, Phys. Rev. B 47, 12727 (1993).
[2] S.A. Sapp et al., Adv. Mater. 11, 402 (1999).
[3] O. Picht et al., J.of Phys. Chem.. C 116, 5367 (2012).
[4] J. Gronefeld, Bachelor Thesis, TU-Darmstadt.
[5] S. Mueller, PhD Thesis, Univ. of Heidelberg.