SCANNING THERMAL MICROSCOPY OF THERMOELECTRIC PULSED LASER DEPOSITED NANOSTRUCTURES

VANIŠ Jan[1,2], ZELINKA Jiří[1], ZEIPL Radek[1], JELÍNEK Miroslav[1], KOCOUREK Tomáš[1], REMSA Jan[1], NAVRÁTIL Jiří[3]

[1]*Institute of Physics AS CR, v.v.i., Prague, Czech Republic, EU*
[2]*Institute of Photonics and Electronics AS CR, v.v.i., Prague, Czech Republic, EU*
[3]*Institute of Macromolecular Chemistry, AS CR, v.v.i., Prague, Czech Republic, EU*

Abstract

New materials with high possible figure of merit ZT are of high interest as a promising candidates for thermoelectric applications such as energy harvesting. Miniaturization of such systems tends toward developing of the suitable characterization method with nanometer resolution ability. In our contribution, we present the development and experimental results of a simple scanning probe microscopy method for the relative thermal conductivity characterization. The possibility of the setup is demonstrated on the set of different thin thermoelectric layers grown from hot pressed targets by pulsed laser deposition on the reference Si substrate. All the measurements were performed on the commercial Veeco Multimode scanning AFM/STM microscope with home developed controller and by using PicoCal Inc. bolometer probes with tungsten resistive path. All the experiments were done in the air at the ambient condition. Additional sample treatment for the measurement will be also briefly described

Keywords: Scanning thermal microscopy, figure of merit, thermoeletric materials

1. INTRODUCTION

Thin layers, multi-layered structures and superlattices are suitable as a starting structures for thermoelectric nanodevices [1]. Knowledge of properties of such structures with lateral resolution in the nanometer scale is crucial from the point of view of nanophysics, nanoelectronics, nanomechanics and nanomedicine. Hence, there is need of techniques able to reach a nanometric spatial resolution. Scanning thermal microscopy (SThM), member of a family of scanning probe microscopies (SPM), shows its abilities since its invention in 1986 [2]. It is based on atomic force microscope (AFM) equipped with a thermal probe to carry out thermal images together with simultaneously obtained contact mode topography image [2,3]. At the beginning, thermocouple probes like AFM cantilever were used, in order to profit from force feedback. Nowadays mainly resistive thermal probes are used. They can operate in passive or active mode. In the passive mode, the temperature of the probe is estimated during scanning by measuring the voltage across the probe by means of the connected bridge. In an active mode, larger currents, which induce Joule heating in the probe, are passed through the probe resistor, inducing Joule heating in the probe. The heat flow between the probe and the sample is influenced by the thermal conductivity of the sample as well as of the thermal resistance at the probe-sample contact area. The active mode can be operated either in constant current mode or in constant temperature mode. In the constant current mode the resistance of the probe changes as a function of the heat flux between the probe and the sample. In the constant temperature mode the feedback loop cause a change of the current through the probe, so that the resistance of the probe does not change during the measurement [4,5]. We introduce a low frequency pulse current mode scanning thermal microscope method for the thermal conductivity evaluation of thin thermoelectric layers. The fast heating response of the cantilever tip on current flow is utilized as a scanning thermal probe. The ability of the suggested method is demonstrated with a set of thermoelectric thin films of different thicknesses prepared by pulsed laser deposition (PLD) on silicon substrates.

2. EXPERIMENTAL RESULTS AND DISCUSSION

For our experiments Bi_2Te_3, $FeSb_2Te$ and $Ce_{0.1}Fe_{0.7}Co_{3.3}Sb_{12}$ thermoelectric materials were used. The starting polycrystalline materials were synthesized from 99.999% starting compounds in evacuated silica ampoules at 1073 K for 48 hours. After verification of the homogeneity of the prepared compound by means of X-ray powder diffraction, the polycrystalline ingot was broken into small pieces with an agate mortar and sieved to obtain particle sizes below 100 µm. The target for PLD deposition of 20 mm in diameter and of 2 mm in height was prepared by the hot pressing method. The measured density of the pressed target reached about 96-98 % of the theoretical expected density.

Layers were grown by PLD in apparatus described elsewhere [5, 6], where several improvements in hardware setup and growth procedure for achieving of smooth surface for every type of material were involved [6]. All layers were deposited on 10 mm x10 mm Si (100) substrate. For each type of material several thicknesses were grown.

For all grown layers crystallinity, stoichiometry, roughness, Seebeck coefficient, in-plane electrical resistivity, and figure of merit (ZT) were measured by conventional analytical methods.

For the thermal characterization of our samples in micron and submicron range using current pulse method we have used commercial SPM - Veeco MultiMode system with NanoScope IVa controller equipped with V version leak resistance ("J") scanner with a scanning range of 180 x 180 µm. For all measurements only one probe with the conductive path resistance of 49.3 Ohm and mean temperature coefficient of 1307 ppm/K was used. Cantilever is of 100 µm width, 2-3 µm thickness and 200 µm length. Over the tip deposited tungsten resistive stripe is two pole terminated. SEM picture of the used probe is shown in **Fig. 1a)**. The probe is produced by Picocal Inc. To increase the system stability and sensitivity, the pulse regime instead of DC mode was used. Our method accounts the thermal characteristics of the used probe types, which have characteristic heating time constant of 0.4 ms (only the tip of cantilever is heated). We assume, that the time constant of the tip is substantially smaller then the rest part of the cantilever. Utilizing this knowledge, we drive the probe with about 400Hz rectangular current pulses of 50% duty cycle (1.2 ms heating up pulse width = 3 x heating time constant). Thus only the tip and the close vicinity area to the tip thermally pulsates, while the rest of the probe remains at its mean constant temperature. The lock in detector evaluates the amplitude of the signal from the differential amplifier, which is proportional to the difference of the tip resistivity during the heating pulses.

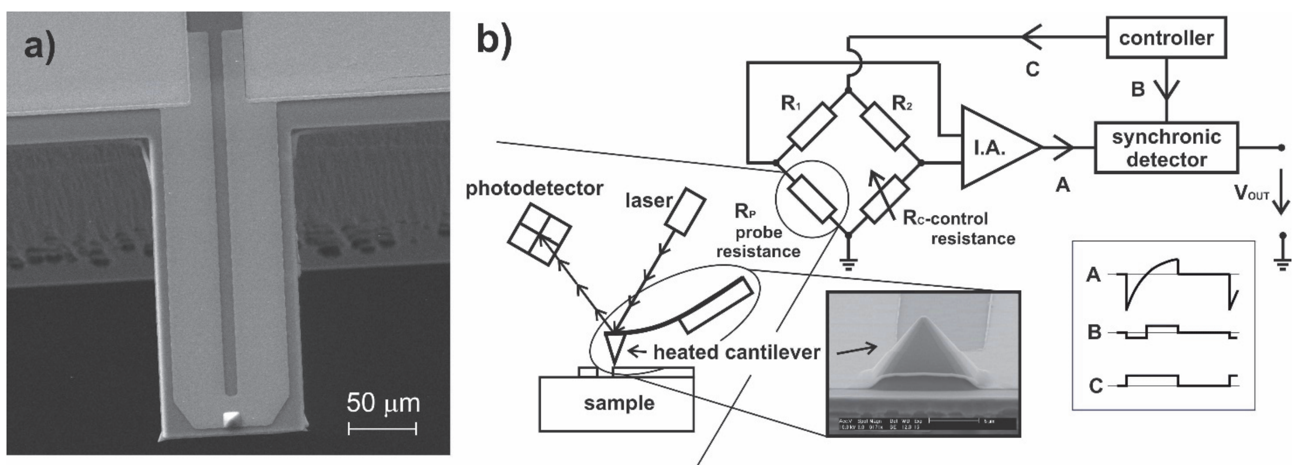

Fig. 1a) SEM image of the used thermal probe, 1b) general setup of the current pulse thermal conductivity measurement

Thus this significantly reduces the DC part of the signal proportional to the ambient temperature drifts. The general scheme of the current pulse thermal conductivity measurement using thermal microscope is shown in **Fig. 1b)**. The output controller voltage is indirectly proportional to the heat drain from the tip. In our case when the input power to the probe is set to 10 mW, it rises the mean temperature of the tip by 15 °C and the pulses

generates an extra 15 °C. Hardware of our Veeco microscope heat up itself to 30°C, so the temperature of the tip pulsates within the range 45 °C-60 °C. The measurements were taken in air at ambient condition.

Although, the utilization of the new instrument in the measuring system increases sensitivity of the measurement for about two orders in comparison with the constant DC current mode and minimizes the influence of ambient interferences on the measurement, a comparison of the properties on each measured sample is possible only with respect to the reference silicon substrate. To obtain such structures, where is a steep edge between the reference silicon layer and the deposited material layer, ion induced milling process controlled by time of flight - secondary ion mass spectrometer (TOF-SIMS) was involved. On each examined layer three 200μm x 200μm craters were milled of directly to the interface. Depth of the interface was determined from the TOF-SIMS depth spectra. All the milling processes were done away from the edges of the sample and Si/layer boundary, thus we expect that evaporated layer has the homogeneous thickness. The whole process was performed in SEM-FIB-GIS-SIMS Lyra TESCAN apparatus, where Ga^+ ion gun was used.

For the atomic force thermal microscope characterization a set of three layers of different thickness were prepared for each material type. The $FeSb_2Te$ layers were 136 nm, 264 nm and 510 nm in thickness, $Ce_{0.1}Fe_{0.7}Co_{3.3}Sb_{12}$ were 146 nm, 300 nm and 738 nm in thickness, and Bi_2Te_3 layers were 155 nm, 415 nm and 900 nm in thickness. The typical image of measured topography and corresponding thermal signal is shown in **Fig. 3** for the Bi_2Te_3 layer, the left-hand side shows the topography image and the right-hand side shows the corresponding thermal signal. The Si and Bi_2Te_3 parts of the sample are also marked in the image. The discontinuity of the thermal signal (-100 μm) on the straight edge is due to the parasitic heat flow through the air surrounding the tip, which we will not describe here. As the samples are prepared on the same substrate and undergo same pre-measurement procedures, while the measurement parameters and conditions are also set to identical values, we can take the value of the relative change of thermal signal on the Si part as a reference.

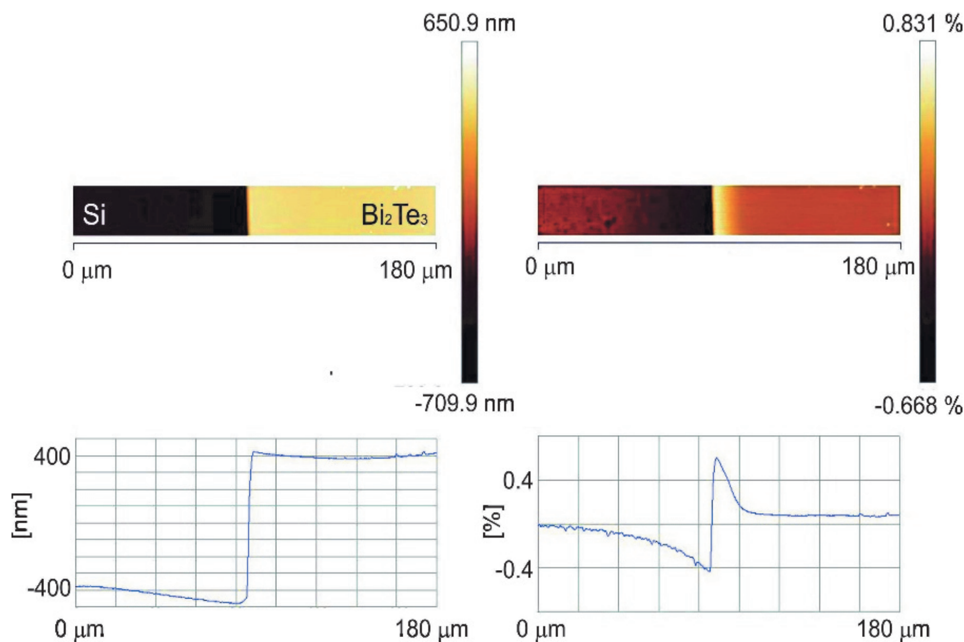

Fig. 2 Surface topography (on the left-hand side) and corresponding relative change of thermal signal (on the right-hand side) with corresponding step profile from the whole area (128 scans) for the edge of the milled crater on the Bi_2Te_3 layer with a thickness of 900 nm

Numerical values of the relative change of thermal signal for Si and Bi_2Te_3 are taken in sufficient distance from the edge, where the signal is equalized. Such normalized thermal signals with respect to the silicon substrate (left part of the image) is shown in **Fig. 3** for Bi_2Te_3 of different thickness (right part of the image).

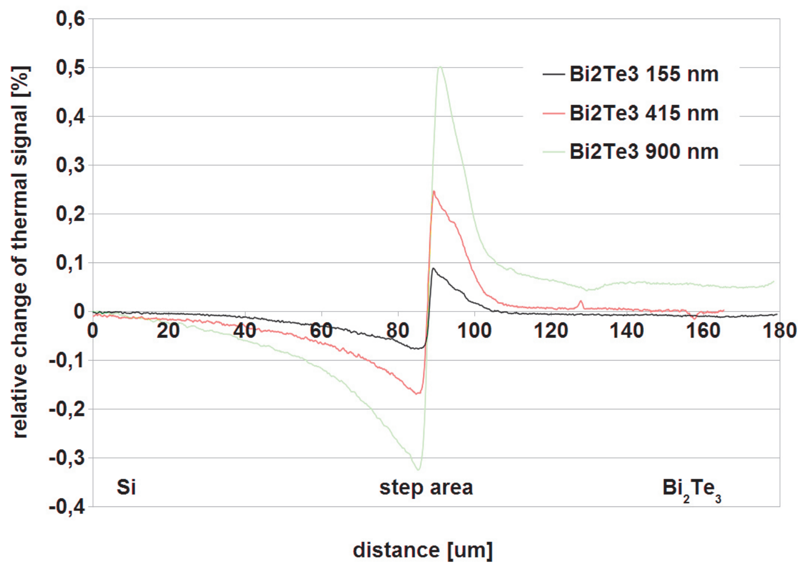

Fig. 3 Response of the thermal signal for the Bi_2Te_3 layers of different thickness equalizes with the respect to silicon layer

Computed difference of these levels is directly proportional to the thermal resistivity of the measured material and its dependence on the thickness of layer for all $FeSb_2Te$, $Ce_{0.1}Fe_{0.7}Co_{3.3}Sb_{12}$ and Bi_2Te_3 materials is shown in **Fig. 4**. The shown dependence on the layer thickness has a linear character for Bi_2Te_3 and $Ce_{0.1}Fe_{0.7}Co_{3.3}Sb_{12}$ whereas for the $FeSb_2Te$, it cannot be estimated because of the value spread.

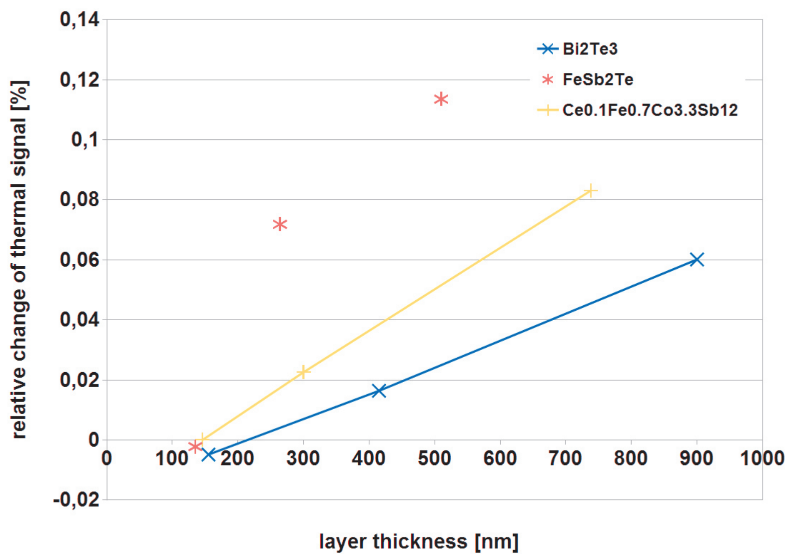

Fig. 4 Dependence of the relative change of the thermal signal on the layer thickness for $FeSb_2Te$, $Ce_{0.1}Fe_{0.7}Co_{3.3}Sb_{12}$ and Bi_2Te_3

3. CONCLUSION

In our contribution we demonstrate the feasibility of the relative thermal conductivity measurement with the new electronic instrument working in pulsed current mode. The specific heating behavior of our Picocal Inc. thermal probes is used. We prove higher sensitivity of the method in comparison with DC method. The nanometer range resolution of $FeSb_2Te$, $Ce_{0.1}Fe_{0.7}Co_{3.3}Sb_{12}$ and Bi_2Te_3 layers with different thickness is shown, where linear dependence of the relative thermal conductivity on thickness was found. To validate our results, additional measurements on different layer thickness are required and a comparison with 3ω method

would be also interesting. The bottleneck of the method is parasitic heat flow through air, which should be cut off by performing the measurements in the vacuum.

ACKNOWLEDGEMENTS

This work was supported by the Grant Agency of the Czech Republic - project no. GA13-33056S.

REFERENCES

[1] VENKATASUBRAMANIAN R.,COLPITS T.S. ,MALTA D.,MANTINI M.,PROCEEDINGS OF THE EUROPEAN THERMOELECTRIC SOCIETY, ST. PETERSBURG, 1995, P.490 UNITED STATES PATENT NO. 5,747,728 (MAY 5, 1998).

[2] WILLIAMS C.C., WICKRAMASINGHE H.K. Scanning thermal prfoiler, Applied Physics Letters Vol. 49, 1986, pp. 1587.

[3] MAJUMDAR A.,LAI J,CHANDRACHOOD M.,NAKABEPPU O.,WU Y.,SHI Z. Thermal imaging by atomic force microscopy using thermocouple cantilever probes, Review of Scientific Instruments. 66, 1995, pp. 3584.

[4] MAJUMDAR A. Scanning thermal microscopy, Annu. Rev. Mater. Sci. 29, (1999), pp. 505-585.

[5] ZEIPL R., JELINEK M.,KOCOUREK T.,REMSA J.,VANIŠ J.,VLČEK M. Properties of Thermoelectric Nanocomposite Bi2Te3 Layers Prepared by PLD, Sensors and Transducers Journal 183(12), 2014, pp. 103-109

[6] REMSA J.,JELINEK M.,KOCOUREK T.,ZEIPL R., NAVRATIL J., Very smooth FeSb2Te and Ce0.1Fe0.7Co3.3Sb12 layers, Proceedings of 34th International Conference on Thermoelectrics in press.