# STRUCTURAL AND THERMOELECTRIC CHARACTERIZATION OF INDIVIDUAL SINGLE CRYSTALLINE NANOWIRES

*Z. Wang[1], M. Kroener[1], and P. Woias[1]*
[1]Laboratory for Design of Microsystems, Department of Microsystems Engineering – IMTEK, University of Freiburg, Germany

## ABSTRACT

We demonstrate the fabrication and initial testing of a novel micromachined **T**hermoelectric **N**anowire **C**haracterization **P**latform (TNCP) which will be applied to measure the thermoelectric properties of a single thermoelectric nanowire. The assembly of the nanowire onto the TNCP is conducted by means of dielectrophoresis (DEP) in combination with a controlled deposition and evaporation of a liquid sample containing nanowires. This paper presents the design of the TNCP with integrated sensors and DEP electrodes, methods of surface modification for a controlled deposition and evaporation and a successful nanowire deposition.

## KEYWORDS

TNCP, thermoelectric nanowires, dielectrophoresis

## 1. INTRODUCTION

Nanowires are becoming more and more attractive for an application in nanoelectronic, optoelectronic and thermoelectric devices [1,2]. Within that trend superior thermoelectric nanowires, made from $Bi_2Te_3$ or $Sb_2Te_3$, are assumed to play a major role in the design of thermoelectric power generators with improved conversion efficiency [3, 4].

The so-called "figure of merit" (denoted as ZT) indicates the thermoelectric efficiency of every thermoelectric material and is formularized as follows:

$$ZT = \frac{\sigma \cdot S^2}{\kappa} \qquad (1)$$

where σ is the electrical conductivity, S the Seebeck coefficient and κ the thermal conductivity of the thermoelectric material. Equation (1) tells us that the ZT value can only be calculated for a nanowire, when σ, S and κ are measured on the same single specimen. The majority of previous studies were made to measure merely one or two of these three parameters, with nanowires formed in bundles or mats [5, 6]. Therefore, our research is focused on developing a novel platform (TNCP) to determine σ, S and κ simultaneously on one single nanowire.

For this purpose, a technique has to be developed that allows (1) to deposit a single nanowire on a specific position of the TNCP and (2) to establish a well-defined thermal and electrical connection. Hence, dielectrophoresis is implemented to direct and move nanowires in a liquid medium by means of electrical fields. This guiding field is generated by applying an AC voltage over specific DEP electrodes on the TNCP. By varying the voltage and frequency, the nanowire behaves quite differently due to the change of external electric field and its interaction with the specimen. To assist this process the evaporation of the surrounding liquid medium is conducted in a controlled manner.

## 2. TNCP DESIGN AND FABRICATION

The TNCP is realized by silicon micromachining. It is composed of two adjacent, symmetric and suspended Si cantilevers with a length of 1000 µm, a width of 100 µm and a thickness of 10 µm, as shown in Fig. 1. The nanowire is deposited between the adjacent tips of the cantilevers, over a gap of 10 µm to 25 µm. The purpose of this setup is to generate a sufficient thermal insulation of the nanowire from the silicon substrate as a prerequisite for a precise measurement of the thermal conductivity κ.

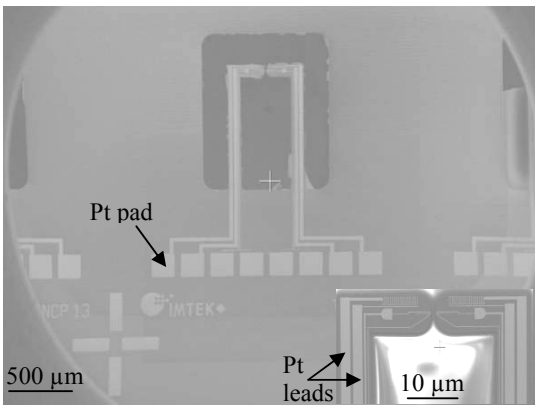


*Figure 1: SEM image of one TNCP on silicon wafer (large picture) and a detail view of the opposite cantilever tips with integrated heaters, temperature sensors and DEP electrodes.*

Each cantilever carries a 200 nm thick, 1.5 µm wide and 570 µm long platinum (Pt) meander. For the Seebeck measurements this resistor serves as a micro-heater to establish a temperature difference between the cantilevers and, hence, over the nanowire. It is also suited to detect the actual temperature on the cantilever tips (Fig. 2). The Pt resistors are connected to 185 µm × 185 µm Pt bond pads on the substrates via 1400 µm long and 30 µm wide Pt leads on the long suspended cantilevers. The Pt leads are fabricated much wider than the resistors to reduce voltage drops and heating effects. Two V-grooves are designed on each cantilever tip via anisotropic etching in order to accommodate the ends of a single nanowire bridging the two cantilevers. The width and depth of the two V-grooves are 2 µm and 1.41 µm, respectively. The distance between the tips of the two cantilevers is fabricated in a range from 10 µm to 25 µm to allow the assembly of nanowires with a different length. Four electrodes are deposited on the bottom of the two V-grooves for the latter four-point measurement of the

electrical conductivity σ and a 3ω approach for the κ measurement. Also, two electrodes are fabricated symmetrically on each cantilever for DEP.

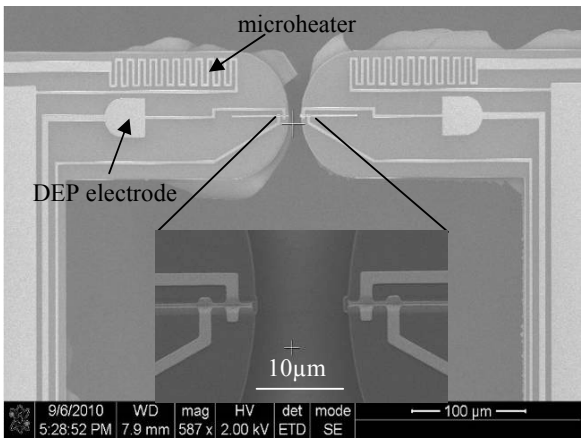


*Figure 2: SEM image of the cantilever tips. Inset: detail view of the V-grooves and the four electrodes set-up for the measurement of σ and κ.*

The TNCP is batch-fabricated by silicon micromachining (Fig. 3). The process uses 100 mm diameter silicon-on-insulator (SOI) wafers with a 380 µm thick handle Si layer, a 1 µm thick buried $SiO_2$ layer and a 10 µm thick device Si layer on top. First, 300 nm $SiO_2$ and 100 nm $Si_3N_4$ are deposited on both sides of the SOI wafer by means of wet thermal oxidation and low pressure chemical vapor deposition (LPCVD), respectively (Fig. 3a). Then two photolithography steps are executed on both sides and the photoresist pattern is transferred to the $SiO_2/Si_3N_4$ layer by reactive ion etching (RIE). The V-grooves and cavities on the surface and the bottom side, respectively, are formed via wet chemical etching with potassium hydroxide (KOH). As $SiO_2$ is also slightly attacked by KOH, tetramethylammonium hydroxide (TMAH), which will precisely etch-stop at the buried oxide layer, is employed to substitute KOH at the end of the bottom-cavity formation (Fig. 3b). Afterwards, hydrofluoric acid (HF) is used to remove the $SiO_2/Si_3N_4$ layers on both sides including the buried oxide layer which is exposed to air (Fig. 3c). Next, wet thermal oxidation and LPCVD are used to grow a new $SiO_2/Si_3N_4$ layer stack on both sides of the wafer in order to compensate layer stress in the cantilevers and to prevent a stress-induced bending of the released cantilevers. After deposition of a 10 nm titanium (Ti) adhesion layer and a 200 nm Pt on the top side by means of radio-frequency (RF) sputtering, the third photolithography step is applied to pattern this metal layer via ion beam etching (IBE), as shown in (Fig. 3d). Another photolithography step is utilized to pattern the wafer surface for the deep reactive ion etching (DRIE) process that shapes the cantilevers (Fig. 3e). Using RIE on the top side, the cantilevers are finally released from the remaining oxide layer and the photoresist is stripped by Diener Tetra oxygen plasma (Fig. 3f).

Approximately 600 chips with dimensions of $2\times3mm^2$ are produced on one SOI wafer. On the diced chips a photoresist cover was applied manually over the cantilever tips. Afterwards the chip surface is coated with a 100 nm thick polytetrafluoroethylene (Teflon) layer (Fig. 3g). After removal of the photoresist the cantilever tips remain hydrophilic, while all other parts of the TNCP surface exhibit a hydrophobic behavior. This treatment considerably facilitates the latter deposition of droplets with nanowires onto the tips of the cantilevers. Otherwise, the droplet is easily attracted to other parts of the TNCP which may hinder the nanowire deposition.

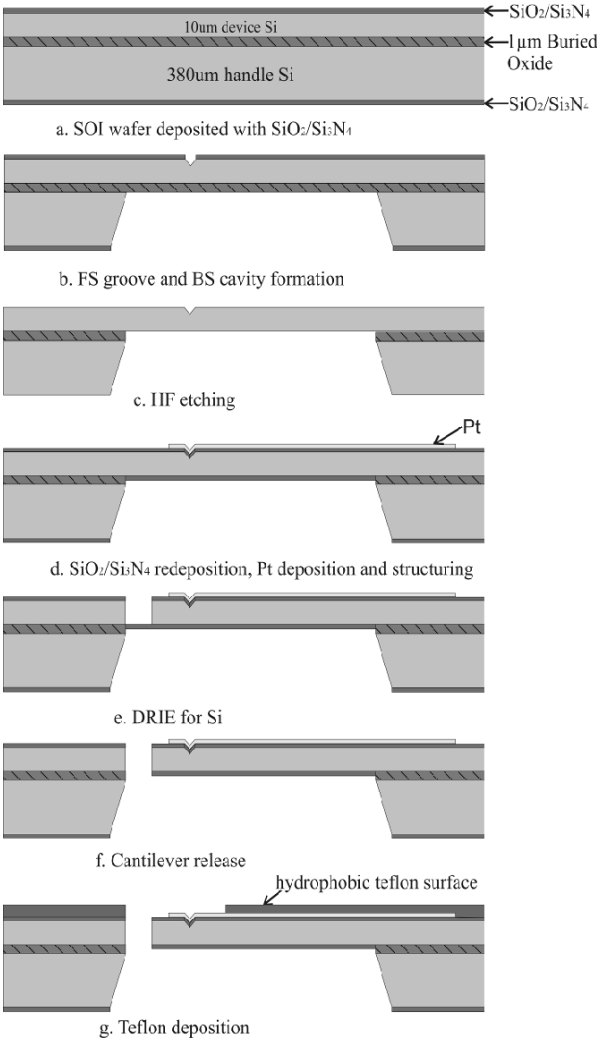


*Figure 3: Fabrication process of the TNCP.*

## 3. NANOWIRE ASSEMBLY

### Dielectrophoresis

The assembly of nanowires by utilizing dielectrophoresis is becoming increasingly popular, as this methodology is proven to have the ability to position nanowires accurately [7-9]. The definition of dielectrophoretic force was first put forward by H. A. Pohl in 1951 [10]. When a neutral object is subjected to a nonuniform electric field, $\vec{E}$, a translational force, $\vec{F}$, is produced which is proportional to $E^2$. In more detail, if an uncharged particle experiences an external electric field,

this will develop an induced dipole moment within the particle. The dipole moment depends on the strength of the applied electric field and the polarizability of the material. Due to the electric field, the induced dipoles are oriented in the direction of $\vec{E}$, so that dielectrophoretic force emerges. For cylindrical particles as assumed for thin, long nanowires, which are suspended in a fluid medium, the dielectrophoretic force is [11]:

$$\vec{F}_{DEP} = \frac{2L\pi r^2}{3}\varepsilon_m \,\mathrm{Re}[K(\omega)]\cdot(\vec{\nabla}\left|\vec{E}\right|^2) \qquad (2)$$

where r and L are the radius and length of the nanowire, respectively, $\varepsilon_m$ is the absolute permittivity of the medium, E is the time-varying applied electric field, and $K(\omega)$ is the Clausius-Mossoti factor for the cylindrically shaped particles as a complex number. The real part of $K(\omega)$ can be expressed as follows:

$$\mathrm{Re}[K(\omega)] = \mathrm{Re}\left[\frac{\varepsilon_p^*(\omega)}{\varepsilon_m^*(\omega)} - 1\right] = \frac{\omega^2\varepsilon_p\varepsilon_m + \sigma_p\sigma_m}{\omega^2\varepsilon_m^2 + \sigma_m^2} - 1 \qquad (3)$$

where $\varepsilon_p$ is the permittivity of the particle and ω the angular frequency of the applied AC voltage. In a set-up with two electrodes on top of a silicon substrate (Fig. 4), the nanowires will be pushed towards the lower electric field gradient, i.e. away from the substrate if $\mathrm{Re}[K(\omega)]$ is negative. For a positive value of $\mathrm{Re}[K(\omega)]$ the DEP is exerting an attractive force towards the regions with maxima of the electric field.

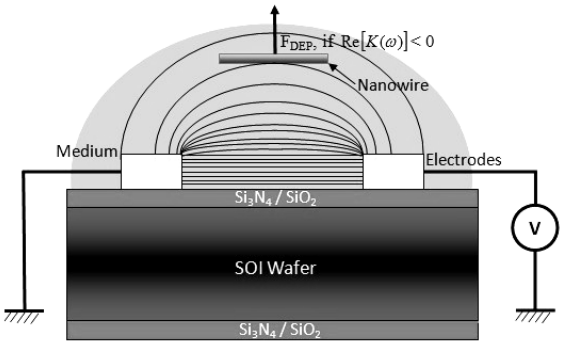


*Figure 4: DEP force on a nanowire in a liquid medium for Re[K(ω)] < 0.*

In our work, dielectrophoretic force is exerted to precisely integrate one single $Bi_2Te_3$ nanowire (Fig. 5) into the 2 µm wide V-grooves at the tips of the cantilevers. The process is assisted by a controlled evaporation of the surrounding medium. The nanowires have a diameter ranging from 200 nm to 300 nm and a length between 30 µm and 40 µm. For the deposition, the nanowires are dispersed in a liquid medium first. A small droplet (50~100 nanoliters) is deposited on the cantilevers. As time elapses, the droplet becomes smaller due to the evaporation that confines the free space for nanowires to move. Meanwhile, an AC voltage is applied to generate DEP and to orient and polarize nanowires. After the droplet is fully evaporated, at least one nanowire is bridging the cantilever tips (see Fig. 6)

Using equation (2) the maximum DEP force on a nanowire is approximately 45 µN. According to equation (3), $\mathrm{Re}[K(\omega)]$ = -0.275 for $Bi_2Te_3$ nanowires.

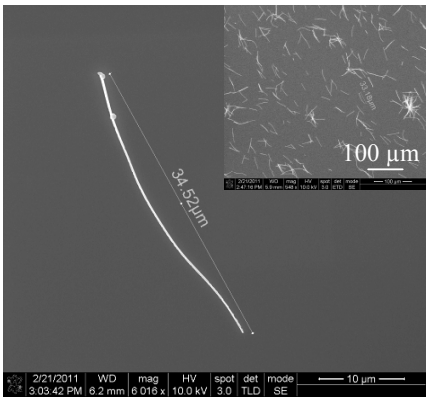


*Figure 5: SEM image of a single $Bi_2Te_3$ nanowire which presumably possesses superior thermoelectric properties. Inset: a large number of nanowires dispersed on one Si wafer.*

This implies that the nanowires will be dragged to regions with lower electric field strength. Therefore, the nanowires are located in the fringe of the liquid droplet with oriented direction parallel to the surface of cantilever and the V-grooves (see Fig. 4). On the first sight this is detrimental for a controlled deposition. However, the evaporation of the droplet will reduce the available free space and force the nanowires to move towards the cantilever tips with a well-oriented direction until they finally are placed over the gap.

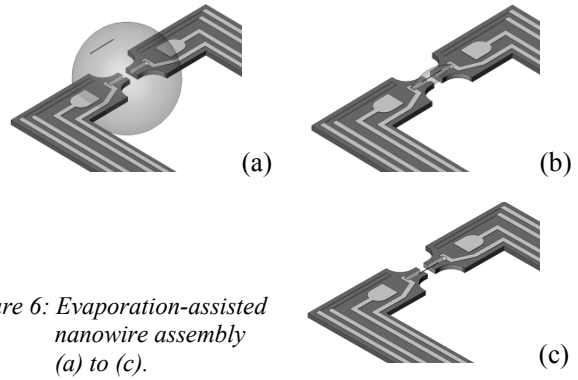


*Figure 6: Evaporation-assisted nanowire assembly (a) to (c).*

**Experimental**

For the deposition process a large number of nanowires are suspended in an aqueous or organic solvent such as isopropanol, ethanol or acetone. The liquid sample is diluted so that nanowires can be separated into smaller fractions. By using a micro-scale pipette with a 200 µm diameter tip, a small droplet (50~100 nanoliters) is supplied onto the TNCP.

After the deposition of one water droplet, it is found that the droplet takes a long time (5 min) to evaporate. This is too long for a controlled nanowire assembly, as it allows the nanowires to move inside the droplet in an uncontrolled way, with all negative side effects, for instance, agglomeration or undesired surface adhesion. Hence, the micro-heaters on the cantilever tips were used to heat up the water droplet with a total applied electrical

power of 5.2 mW to reduce the dry-out time to 30 seconds. During the heating, some bubbles are observed, which is presumably due to the electrolysis of water. As seen in Fig. 8, the final confinement of the nanowires is taking place as expected. The droplet volume before evaporation (25 s) is approximately 10 nl.

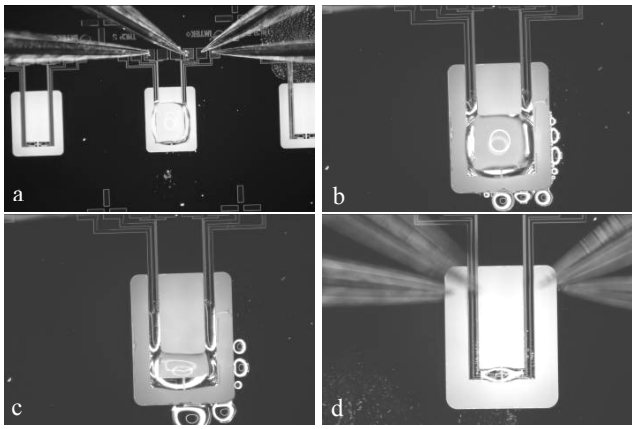


*Figure 8: Dry-out process of a 80 nl water droplet, a: 0 s, b: 5 s, c: 15 s, d: 25 s.*

The deposition of a nanowire cannot be successful in all experiments, as the number of nanowires per droplet, their aggregation state or undesired depositions at unwanted positions cannot be excluded. However, within a series of 200 experiments, about 10% were successful with one nanowire situated in the V-groove as requested. This justifies the efficiency of the combined evaporation-DEP process. Once the nanowires touch the surface of TNCP, they seem to adhere firmly to the surface and no release of nanowires was observed in all experiments. It was found that an applied AC voltage in the range between 5 V and 8 V, frequency from 100 kHz to 8 MHz yield the best results for the DEP process.

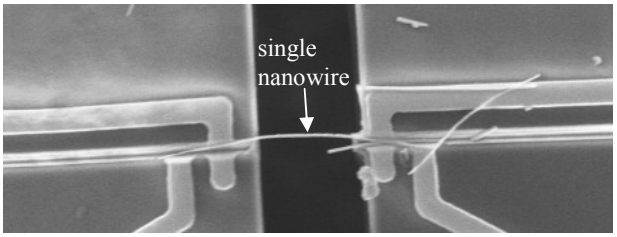


*Figure 9: Result of a successful experiment, with a single nanowire bridging the two cantilever tips (DEP voltage:6 V, DEP frequency: 8 MHz*)

After the end of the experiment it is not easy to determine the success, as the nanowire is not visible in an optical microscope. However, it turned out that the evaporation behavior during the deposition process gives an indicator for the success. From that a method has been developed to distinguish the nanowire existence in the V-groove. With nanowires in the V-groove the water will be trapped and will evaporate along the nanowires due to adhesive forces (see Fig. 8d). With no nanowires in the V-grooves, the water droplet would randomly bridge other spots of the cantilever tips, i.e. not the V-grooves, or even coalesce at one of the cantilever tips.

## 4. SUMMARY AND FURTURE WORK

A novel **T**hermoelectric **N**anowire **C**haracterization **P**latform (TNCP) has been designed, fabricated and successfully tested with respect to the critical nanowire assembly process. DEP in combination with a controlled sample dry-out has been employed to assemble nanowire from a liquid medium onto the TNCP. In the future, ohmic contact between the nanowire and the TNCP will be generated by SEM e-beam deposition and σ, S and κ will be measured for the single nanowire which is integrated on TNCP.

## REFERENCES

[1] Y. Liu, R. E. Allen, Phys. Rev. B 52, 1566, 1995.
[2] A. Svizhenko, A. Balandin, S. Bandyopadhyay, J. Appl. Phys. 81, 7297, 1997.
[3] W. Wang, F. Jia, Q. Huang, J. Zhang, "A new type of low power thermoelectric micro-generator fabricated by nanowire array thermoelectric material", Microelectronic Engineering, 77, 223-229, 2005.
[4] H. Linke, T. E. Humphrey, M. O´Dwyer, "Energy-specific Equilibrium in Nanowires for Efficient Thermoelectric Power Generation".
[5] D. S. Choi, A. A. Balandin, M. S. Leung, S. W. Chung, A. Khitun, K. L. Wang, "Transport Study of a Single Bismuth Nanowire Fabricated by the Silver and Silicon Nanowire Shadow Masks", Appl. Phys. Let. 89, 141503, 2006.
[6] L. Shi, D. Li, C. Yu, W. Jang, D. Kim, Z. Yao, P. Kim, A, Majumdar, "Measuring Thermal and Thermoelectric Properties of One-Dimensional Nanostructures Using a Microfabricated Device", Journal of Heat Transfer, Vol. 125, 881, 2003.
[7] E. M. Freer, O. Grachev, X. Duan, S. Martin, D. P. Stumbo, "High-yield self-limiting single-nanowire assembly with dielectrophoresis", Nature Nanotechnology, Vol 5, 2010.
[8] S. Raychaudhuri, S. Dayeh, D. Wang, E. T. Yu, "Precise Semiconductor Nanowire Placement Through Dielectrophoresis", Nano letters, Vol. 9, No. 6, 2260-2266, 2009.
[9] H. W. Seo, C. Han, S. O. Hwang, J, Park, "Delectrophoretic Assembly and Characterization of Individually Suspended Ag, GaN, $SnO_2$, and $Ga_2O_3$ nanowires", Nanotechnology 17, 3388-3393, 2006
[10] H. A. Pohl, K. Pollock, J. S. Crane, "Dielectrophoretic Force: A Comparison of Theory and Experiment", Phy. Bio. Sciences Ltd., 1979.
[11] H. Morgan, N. G. Green, "Dielectrophoretic Manipulation of Rod-shaped viral particles", J. Electrostatics 42, 279, 1997.

## CONTACT

*Z. Wang,
tel: +49-761-203-7475, e-mail: zhi.wang@imtek.de