

# FINAL PUBLISHABLE REPORT

Grant Agreement number Project short name Project full title

#### 19ENG05

NanoWires

High throughput metrology for nanowire energy harvesting devices

Project start date and duration:		01 September 2020, 36 months			
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Project website address: https://www.ptb.de/empir2020/nanowires/home/					
Internal Funded Partners:	External Funded Partners:		Unfunded Partners:		
1. PTB, Germany	8. Aalto, Finland		17. CSI, France		
2. CMI, Czechia	9. CNRS, France				
3. DFM, Denmark	<ol> <li>ELECTRO, United Kingdom</li> <li>GET, Austria (withdrawn 31 August 2021)</li> </ol>				
4. GUM, Poland					
5. INRIM, Italy					
6. LNE, France	12. PWR, Poland				
7. VSL, Netherlands	13. TCD, Ireland				
	14. TUBS, Germa	any			
	15. UAB, Spain				
	16. QDM, Germa 2021)	ny (joined 1 Jan			
Linked Third Parties: 18. ECL, France (linked to CNRS)					

Report Status: PU Public

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The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States



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## 1 Overview

Energy harvesting from renewable sources (solar, heat and movement) is a prominent solution to create small amounts of electrical energy in areas of difficult access, and energy harvesting devices have much potential to address our world energy problems. Nanowire (NW) based energy harvesting systems have achieved encouraging progress, but due to nanometre (nm) dimensions of the wires and large size (m<sup>2</sup>) of the devices, they also bring challenges for testing and characterisation. Average properties of energy harvesting devices can be measured, but a quantitative link and correlation between the performance of single NWs and that of the overall device is lacking. This project aimed to develop reliable and high throughput metrology for the quality control of NW energy harvesting systems. Within the frame of this project, hybrid traceable metrology was developed for high throughput nanodimensional, nanoelectromechanical and thermoelectrical characterisation of NW devices made of innovative nanomaterials. All these innovative results will help the nanometric energy harvesting industry including developers and manufacturers in further supplying of more efficient and reliable products.

## 2 Need

Limited fossil fuel-based energy resources and their negative effect on the environment have resulted in enormous efforts being made over several decades to make energy supply and consumption more sustainable. Scavenging energy from renewable sources like solar, waste heat and mechanical movement is seen as a prominent solution to our world energy problems.

Over the past two decades, major efforts have been made to develop energy harvesting devices from macro and microscales down to nanoscale. Due to their extremely small physical size and high surface to volume ratio, NW based energy harvesting systems, including photovoltaic solar cells, thermoelectrical and electromechanical energy nanogenerators, have gained tremendous interest and encouraging progress has been achieved. In particular, it has been confirmed that the efficiency of NW solar cells can be enhanced from 17.8 % currently to its ultimate limit of 46.7 % by means of nanophotonic engineering.

While novel designs and materials for various energy harvesting devices indeed offer many potential benefits, they also bring challenges for testing and characterisation. For example, the quantitative link and correlation between the performance of a single NW and that of the overall device is still missing. Moreover, no reliable metrology for large area NW arrays (from  $cm^2$  to several  $m^2$ ) with diameters between 50 nm and 1  $\mu$ m is currently available. Quality control of these energy harvesting systems is therefore highly challenging, and high throughput metrology is necessary, which requires the development of traceable measurement methods and models for the characterisation of NW energy harvesters, solar cells and devices.

## 3 Objectives

The overall goal of this project was the traceable measurement and characterisation of energy harvesting devices based on vertical NW. The specific objectives were:

- To develop traceable measurement methods for high throughput nanodimensional characterisation of NW energy harvesters (> 10<sup>8</sup> NWs/cm<sup>2</sup>) including 3D form (cylindrical, prismatic, pyramidal) and sidewall roughness.
- To develop traceable measurement methods for high throughput nanoelectrical characterisation of semiconductor NW solar cells using conductive AFM for current-voltage in the current range 100 fA to 1 mA, SMM for doping concentration variation (between 10<sup>15</sup> and 10<sup>20</sup> atoms/cm<sup>3</sup> with an accuracy better than 10 %), and MEMS-SPM for lateral resolution (< 50 nm).</li>
- To develop and validate traceable measurement methods and models for high throughput nanomechanical characterisation of NW devices, and electromechanical energy harvesters taking into account local bending and compression of NWs including the development of a traceable MEMS-SPM (< 10 pm depth resolution) for fast simultaneous nanomechanical and electrical measurement of semiconductor and polymer piezoelectric NWs.
- 4. To develop and validate traceable measurement techniques for thermoelectrical characterisation, based on fast areal thermal imaging, of NWs (thermal conductivity lower than 10 W/(mK) with an uncertainty < 10 %) under different scanning speeds and tip-surface contact.



5. To facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain, standards developing organisations (IEC TC 113 and IEC TC 82) and end users (solar cell and energy generator manufacturers).

# 4 Results

#### Objective 1

# To develop traceable measurement methods for high throughput nanodimensional characterisation of NW energy harvesters (> 10<sup>8</sup> NWs/cm<sup>2</sup>) including 3D form (cylindrical, prismatic, pyramidal) and sidewall roughness.

Although low-cost and high device efficiency has recently been satisfied with random NW arrays, successfully demonstrating first small NW solar modules, the average length, diameter and density of the arrays has to be controlled to achieve an improved performance. The development of methods enabling accurate determination of all statistical parameters (mean values and standard deviations), requires suitable test structures based on arrays of Si NWs. For photonics applications, catalyst-free growth of ZnO or GaN NW arrays were proposed, i.e., using epitaxy.

Fabrication of high-density ZnO NW arrays at much lower cost and thus a much higher attractivity for energy harvesting applications is usually done by self-organised growth from a chemical vapour source or employing hydrothermal methods. For this, optimised process conditions are necessary to obtain good vertical alignment and separation of the single NWs. Regardless of the fabrication method and the type of NW arrays used, the intended performance of the NW arrays for photovoltaic applications is crucially dependent on an accurate and efficient metrology of geometrical structure parameters (length, diameter, edge roughness, orientation) and order parameters such as mean average length and diameters, density and orientation distribution of the coordinated nanosystem. Individual structures can be accurately and easily characterised using local microscopic methods such as AFM or SEM. For characterisation of larger arrays, special microscopy tools e.g. long-range AFM have been developed. However, these have severe drawbacks in terms of (slow) speed, possible contamination or deterioration of the nanostructures and allow only for a sparse sampling of the individual nanostructures. Efficient large area metrology methods are required to support the development and the manufacturing process for the intended commercial applications.

#### • Fabrication of NW array artefacts

In order to achieve this objective, the work was divided into several tasks and firstly the consortium was working on the design and fabrication of the nano arrays with doping concentration  $10^8$  NWs/cm<sup>2</sup>. Certain sample conditions such as uniformity of the NWs had to be met for the best results. This condition is quite challenging when the fabricated NWs are approaching 1 µm in length. Therefore, for this project it was decided to reduce the height of NWs to less than 400 nm and fabricate them as uniform and parallel to each other as possible while maintaining the fixed period in x- and y-axes as shown in Figure 1. The target of fabrication of NW array artefacts with a density >  $10^8$  NWs/cm<sup>2</sup> has been met.





Figure 1. Fabricated Nanowires. (a) Nanopatterned masks of Cr dots (thickness  $\sim$ 30 nm, diameter  $\sim$ (224 ± 6) nm and pitch  $\sim$ 600 nm, SEM top-view), inset is the magnified view of a single mask-dot, (b) cryo-DRIE-fabricated Si NWAs (diameter  $\sim$ (205 ± 3) nm and pitch  $\sim$ 600 nm, height  $\sim$ 360 nm, 30°-tilted SEM view), (c) SEM top-view of (b), (d) cryo-DRIE-fabricated Si NWAs (diameter (108 ± 4) nm and pitch  $\sim$ 500 nm, height (156 ± 4) nm, 30°-tilted SEM view).

 Traceable high throughput methods for the measurement of sidewall roughness, vertical angle and form deviation of NWs.

For the NW-arrays, different parameters such as structure size, period, displacement, form, orientation, aspect ratio are crucial for the final performance of the PV device. Therefore, in this project optical methods to characterise different parameters by analysis of the different sampling approaches in combination with sensitivity and uncertainty consideration were developed. Fast optical ensemble measurements of the structures under test were quantified and the capabilities to characterise the relevant parameters of the Si NW arrays were investigated. The nanowires were designed in such a way that the measurements could be performed by multiple contact-based and non-contact measurement techniques. NWs with various aspect ratios were fabricated by Electron Beam Lithography as well as self-assembly and metal-assisted chemical etching. As a second step, the fabricated NWs were measured by SEM, AFM, optical coherent and partially coherent Fourier scatterometry, Mueller ellipsometry, etc. These different types of measurement techniques were combined to determine the geometrical parameters such as the diameter, the height, and the pitch of the NWs. The diameter of nanowires was measured by partners with 5-10 nm uncertainty, while pitch and height could be measured with uncertainties of 3 nm and 2 nm respectively. Also, partners provided SEM measurements where the sample height and diameter were measured with 3-4 nm uncertainty. Partners successfully measured samples by scatterometry and retrieved geometrical parameters by using apriori information and the hybrid metrology approach. To measure the sidewall roughness the individual NWs fabricated were traceably measured by the partners using AFM in an international comparison organised by the partners. The hybrid metrology approach was implemented by partners supplying combined measurement results performed by AFM which is dedicated to dimensional measurement, resiscope dedicated to electrical properties measurements, SThM dedicated to thermal properties measurements and SMM dedicated to electrical properties measurements.

#### Hybrid metrology

This objective was achieved by the collaboration of the partners when the samples were measured by multiple instruments available in different institutions. Contact and optical measurement technique experts exchanged their knowledge and created NWs measurement methodologies presented in publications. Another output of this project is the design of the NWs suitable for multiple measurement techniques. Also, it was demonstrated that the samples can be fabricated by two different techniques. The combination of advanced AFM and SEM metrology together with sophisticated optical metrology tools provided, for the first time, access to 3D geometrical form and size of the nanowires both locally (AFM, FIBSEM) as well as globally (i.e. scatterometry and MME). Efficient modelling capabilities were developed to investigate the link between electromagnetic action and structural properties. Partners have demonstrated rigorous evaluation with the differential evolution method of the geometry parameters diameter, height, and pitch in principle on a sample with sufficiently ideal



nanowires. Since the simulations were very time-consuming, the more efficient model such as Bayes optimisation, has been successfully tested as a several orders of magnitude faster method.

Therefore, as a set of demonstrator NW arrays made of different materials (e.g. Si, ZnO and GaN) with diameters below 100 nm, cylindrical shape, aspect ratios between 20 and 100, densities between 10<sup>8</sup> NWs/cm<sup>2</sup> and 10<sup>9</sup> NWs/cm<sup>2</sup> and sidewall roughness ranging from nm to tens of nm have been developed, the overall objective was successfully achieved.

#### Objective 2

To develop traceable measurement methods for high throughput nanoelectrical characterisation of semiconductor NW solar cells using conductive Atomic Force Microscopy (AFM) for current-voltage characteristic in the current range 100 fA to 1 mA, Scanning Microwave Microscopy (SMM) for doping concentration variation (between 10<sup>15</sup> and 10<sup>20</sup> atoms/cm<sup>3</sup> with an accuracy better than 10 %), and Micro-Electro-Mechanical Systems - Scanning Probe Microscopy (MEMS-SPM) for lateral resolution (< 50 nm).

Objective 2 can be subdivided in two parts, the first dedicated to I-V measurements, the second focused on doping concentration measurements.

# Objective 2.1: Traceable measurement methods for current-voltage (I-V) measurements on NW samples using C-AFM or a MEMS-SPM system

This objective deals with the traceable measurements of I-V characteristics to be performed on individual NW junctions enabling the accurate determination of key photovoltaic parameters, short circuit current *l*<sub>sc</sub>, open circuit voltage *V*<sub>oc</sub>, fill factor, and efficiency. These characterisations should have to be performed under a calibrated illumination that will be focused on a bench of NWs. In addition, I-V characteristics measurements carried out on pure n-doped and p-doped NWs were planned to provide reliable data of two material parameters, the carrier density and mobility. To insure traceable and reliable datasets of all these key parameters required identification of main error sources on the I-V characteristic measurements induced by environmental conditions, used instruments *etc*, and investigation on the corresponding uncertainty components as well as on the repeatability and reproducibility. The ultimate and challenging objective was to compare the datasets obtained on individual photovoltaic NW junctions and those measured on the overall photovoltaic NW junction array. The following section shortly describes the various NW samples fabricated by the partners. The next sections present the implemented experimental set-ups, the elaborated measurement protocols, the main measurement results, identification of error sources and a summary of the key outputs.

#### • NW samples: from pure doped NW to NW junctions

Arrays of pure n-doped and p-doped NWs from GaAs were fabricated by Molecular Beam Epitaxy on silicon substrates using the Vapor Liquid Solid (VLS) growth method at CNRS-INL. A series of p-doped and n-doped NWs were grown and then encapsulated in a Benzocyclobuten (BCB) matrix for further characterisation. In order to achieve a good electrical contact the BCB matrix was then etched by reactive ion etching and a chemical HCl etching was applied before the electrical measurements. Aalto also fabricated Si and Ge NW samples. Each sample type was prepared with and without atomic layer deposited (ALD) Al<sub>2</sub>O<sub>3</sub> layer for C-AFM and SMM characterisation. These NWs were then embedded into an insulating layer by CNRS-C2N.

On the one hand, axial GaAs p-i-n NW junctions were fabricated by CNRS-INL using VLS method. On the other hand, axial GaN p-n NW junctions were fabricated by TUBS using metal-organic vapor phase epitaxy (MOVPE) growth techniques. To better understanding their properties and offering samples for measurements under various conditions for comparison, free-standing mushroom-like GaN NW arrays of two types were fabricated, the first type for C-AFM measurements and the second type, suitable for measurements at microscale using a probe station.

#### • Experimental set-ups for photovoltaic measurements

Various set-ups were implemented by the partners. LNE has used a C-AFM from CSI (nanoObserver) fitted with a Resiscope module covering current ranges from fA to  $\mu$ A. LNE has designed, fabricated and implemented a homemade light source composed of LED nano strips suitable for any kinds of AFM. The LNE AFM system has also been equipped with a calibrated SIMSA solar simulator light source from SliteSource. LNE has benefited from the support of CNRS by using their own C-AFM from Bruker (Dimension ICON AFM). In addition to this AFM, CNRS has also used a complete AFM set-up from CNRS-IPVF (Institut Photovoltaique IIe de France) fitted with a fully characterized solar simulator light source. DFM has performed their



measurements using a metrological AFM from Park Systems (NX-20) with different working modes (Electrostatic Force Microscopy – EFM, and Kelvin Probe Force Microscopy – KPFM, etc). At GET/QDM, all measurements have been performed with the FusionScopeTM (Quantum Design), a combined AFM and scanning electron microscope (SEM) in one system.

Besides, for their measurements, GET/QDM has fabricated 3D nano-printed conductive probe tips that have been characterised on standard conductive test samples. Conductive diamond AFM probes of Berkovich type were fabricated by TCD to be used for measurements involving the PTB MEMS based SPM system. Their electrical properties were characterised by LNE. C-AFM experiments showed high resistance values (up to 440 M $\Omega$ ), which depends largely on the number of consecutive I-V sweeps. Second, the work function of the probes was estimated using frequency-modulated KPFM measurements. The shape dependence of the probes' work function was assessed by performing FM-KPFM scans at different angles.

Moreover, an experimental set-up has been especially implemented at LNE to carry out I-V measurements at microscale on GaN NW junction arrays from TUBS under UV illumination. This set-up was composed of a twoprobes station (Cascade Microtech MPS150) coupled to a dedicated small current measurement circuit and equipped with a deuterium UV light source.

#### • MEMS-SPM for high throughput nanoelectrical characterization of NW samples

A specific experimental development was to implement the adaptation of the MEMS system developed by PTB to the LNE C-AFM taking advantage of its expected performance (high speed for lateral resolution below 50 nm for a scanning speed *v*<sub>lip</sub> up to 1 mm/s) to perform high throughput electrical measurements on NW samples. Assembly of a C-AFM tip into the passive gripper of the MEMS-SPM for a commercial AFM has been intensively discussed between LNE and PTB, leading to a final design to adapt the MEMS to the LNE AFM system. The new adapted support was fabricated by LNE and the mechanical mounting to the AFM system was successfully achieved. Unfortunately the further steps which consisted of connecting the MEMS output signals for feedback control and current measurements through the internal electronics of the C-AFM system and with the help of external current amplifiers demanded too much efforts to LNE and PTB to be achieved in the remaining period of the project. Instead their efforts were focused to improve the PTB MEMS-SPM system in current measurements using a LNE reference sample recently developed in another project (EMPIR 20IND12 Elena). Tests are on-going for final validation and will be completed out of this project.

#### • Measurement protocols

A first protocol has been jointly drawn-up by DFM and LNE to clean the GaAs NW samples before using them with AFM. Another protocol has been put in place by LNE to investigate the effects of applied forces, contact time, scanning speeds and friction on different probes, such as commercial full platinum probes and new diamond probes fabricated by Adama and provided by PTB. The main conclusion of these tests was that the tip's work function decreases upon wearing and the scan direction dependency is related to wearing-induced asymmetry at the tip apex. Finally, some recommendations have been pointed out by the partners to perform C-AFM measurements on NWs. They concern (i) the environment control (reducing relative humidity for retarding oxidations, reducing the temperature inside the AFM enclosure to improve stability), (ii) the scan and operation modes (perform one large scan area to identify multiple conducting NWs, combine to EFM/KPFM), (iii) point&shoot (on the single large area scan: select different positions for all NWs of interest, run automated I-V curves at all positions).

#### • Results on I-V characteristics on single pure n-doped and p-doped NWs

The goal of these measurements was to determine the carrier concentration and mobility of the NWs. To this end, pure p-doped GaAs NWs fabricated by CNRS-INL were jointly measured by CNRS, DFM and LNE and pure p-doped and n-doped Si NWs fabricated by Aalto were measured by GET/QDM. These measurements did not allow one to get significant I-V curves from which the observation of space-charge-limited current regime was expected. Therefore, it was not possible to extract the carrier density and mobility. However, these results show that a comprehensive comparative analysis of EFM (or KPFM) and C-AFM done with the same probe on the same spot is very necessary. This would potentially allow to use EFM to identify the conducting wires: very beneficial to overcome the problem of local oxidation. In addition, reference marking would be needed to compare the same NWs on the same sample shared between partners.

#### • Results on I-V measurements on NW junctions in dark and under illumination

At first, measurements were performed on arrays of not-passivated and passivated GaAs p-i-n junctions NWs fabricated by CNRS-INL using KPFM techniques to validate that these devices are photovoltaic. These measurements were performed in darkness and under illumination in Peak Force KPFM mode on Dimension



ICON AFM at CNRS-GeePs. The small differences on the open circuit voltage  $V_{OC}$  values between DARK and LIGHT show that there is no photovoltaic effect on these devices. The results also show that the matrix has a response close to the values of the NWs. From these results, it is clear that it is not possible to measure the expected data ( $I_{SC}$ ,  $V_{OC}$ ,  $\eta$ ). However, it is possible to check whether they behave like a diode using the Resiscope approach. Resiscope measurements were thus carried out at CNRS-GeePs on these same samples, in particular after a deoxidation treatment performed by LNE. This treatment enabled the correlation of the topography with the electrical mapping at various locations in the sample. Diode behaviours and a pseudo photovoltaic effect were observed, this pseudo photovoltaic effect pointing out a  $V_{OC}$  with no  $I_{SC}$ . The observation that the I-V curves do not overlap raises a number of questions, in particular whether the first voltage sweep does not induce a change in the mechanical/electrical properties of the device. The observed loss of mechanical/electrical contact between the AFM tip and the device could be interpreted as an open-circuit device. These measurements point out how difficult it is to measure I-V on nanodevices, and that there is still a need to be able to carry out a large number of tests to identify the reasons that lead to different I-V curves during a measurement procedure.

Not originally planned in the project but to get a chance to observe photovoltaic properties on NW junctions, LNE has performed I-V measurements at the micrometer scale on GaN p-n junction NWs especially fabricated by TUBS. Again, no photovoltaic effect was observed on any NW, *i.e.* no *V*<sub>OC</sub> and no *I*<sub>SC</sub> but instead variable photoconductive effect of UV illumination with a wide dispersion of results not correlated to NW diameters and variable repeatability according to the NW under test. Hysteretic curves, ramping speed effect and possible threshold voltage above which photoconductive properties of the NW breakdown or disappear have been observed. However, the significant point common to all NWs lies in the observation of exponential variation above 1 V. This has allowed one to extract ideality factor values larger than 2 which could originate from trapassisted tunneling and carrier leakage.

#### • Measurement errors and corresponding uncertainties

It was planned to identify the main error sources which have to be taken into account for the determination of the key photovoltaic parameters. It was expected that these sources would be due to C-AFM instrumentations (applied force, leakage current, laser beam), tip quality (shape, coating, robustness), tip-NW contact (electrical resistance, surface, nature) and environmental conditions (humidity, temperature). Because of lack of photovoltaic NW junctions, efforts have been spent mainly on the instrumentation itself. A significant error source is the parasitic illumination coming from the red laser of the AFM. This has been evidenced by CNRS-GeePs from C-AFM measurements performed on locally doped nanojunctions provided by CNRS-LPICM. Indeed, the red laser induced *I*<sub>SC</sub> and *V*<sub>OC</sub> values not expected in usual measurements conditions without illumination. Therefore, it will be necessary to evaluate the effect of the laser on the photovoltaic NWs, particularly for dark characterisations. Moreover, the measurements have shown an improving electrical contact by increasing tip force (100 nN to 500 nN). Regarding instrumentation, the other main error sources come from the I-V measurement circuit itself (low-noise current amplifier, voltage source). The best way to identify these errors and estimate the corresponding uncertainties implies the use of reference samples. This has been jointly done by LNE and CNRS-GeePs, using a multi resistance wide range resistance standard, newly developed in the EMPIR project 20IND12 ELENA and leading to uncertainties of a few percents.

#### • Summary

The objective of performing traceable measurements of I-V characteristics on individual NW junctions with C-AFM techniques and then providing reliable datasets of photovoltaic parameters of NWs turn out too difficult to be achieved within this project. This matter of fact originates to the highly challenging aspect in fabricating working photovoltaic NW junctions. From a multitude of technologies and materials in the design of NW photoelectric devices reported in the literature, only a few leads to high performance devices, *i.e.* efficiencies reaching 15 %. In this project, various NW samples were fabricated but no photovoltaic properties could be observed. Nevertheless, thanks to these samples, the works performed here can be considered as a first step for the metrological investigation of photoelectric NWs and provide some good insights of metrological developments to support the NW technologies in the photoelectric domain. The project has pointed out the high relevancy of the use of non-contact C-AFM techniques, like EFM and KPFM as complementary techniques to the contact C-AFM in the detection and characterization of photoelectric NW. It has been shown that the parasitic illumination coming from the red laser of the AFM is a significant error source in photoelectric measurements. It is worth noting the interest to extend measurements on NW junctions at microscale (using a probe station). They can reveal parasitic effects and error sources which undoubtedly exist at nanoscale but are much easier to be investigated at microscale (because of no issue due to the AFM tip).



# Objective 2.2: Traceable measurement methods for doping concentration measurements on NW samples using SMM

This challenging objective consisted in measuring the doping concentration values with a calibrated SMM scanning the top surface of NWs in contact mode with an expected uncertainty below 10 % and to compare to values determined by Cathodoluminescence (CL) and Electron-beam induced current (EBIC) on similar NWs. To this end, SMM calibration methods were investigated, relying on fabricated fit for purpose 2D reference multilayer samples. Lot of measurements were performed on the same NW samples investigated for objective 2.1 (pure doped NWs, NW junctions) and include not only SMM, CL and EBIC techniques but also Photoluminescence (PL) and contactless CV techniques. The latter were carried out on NW junctions to investigate NW passivation layer properties and to correlate with data obtained from I-V measurements.

The following sections give a description of the multilayer reference samples fabricated by partners and used to calibrate the SMM, present the main measurement results (validation of SMM calibration methods, doping concentration measurements with SMM, CL, EBIC, PL and CV techniques), then address questions of error sources and related uncertainties followed by a summary of key outputs.

#### • Multilayer reference sample for SMM measurements

CNRS-INL has grown two Be p-doped GaAs (001) multilayer samples with a staircase-like dopant structure. The first one consists of height doped layers with dopant levels ranging from 1.10<sup>16</sup> cm<sup>-3</sup> to 1.10<sup>19</sup> cm<sup>-3</sup> while the second sample consists of four layers with dopant levels ranging from 1.10<sup>18</sup> cm<sup>-3</sup> to 2.10<sup>19</sup> cm<sup>-3</sup>. One n-doped GaAs multilayer sample has also been investigated. This sample consists of height Si n-doped GaAs layers with dopant levels ranging from 1.10<sup>16</sup> cm<sup>-3</sup> to 1.10<sup>19</sup> cm<sup>-3</sup>. The design of the multilayer samples was based on requirements provided by LNE. For each sample, an intrinsic GaAs spacer of 200 nm has been added between each doped layer to obtain a better dopant profile since it stops the dopant diffusion. Each doped layer has a thickness of 600 nm. Besides, CNRS-C2N has grown doped GaN reference samples on Si(111) with similar staircase-like dopant structure with concentration ranging from 7.10<sup>15</sup> cm<sup>-3</sup> to 3.10<sup>19</sup> cm<sup>-3</sup> for n-doping.

#### • Doping concentration calibration using SMM on doped multilayer samples

The SMM calibration method based on modified Short Open Load (mSOL) method was demonstrated on pdoped GaAs multilayer reference samples. A good agreement within  $\pm 10\%$  was found for the relative dopant concentration ratios between layers using SMM measurements performed at LNE and Secondary Ion Mass Spectroscopy (SIMS) measurements carried out by Probion Company. For instance, the calibration seems to have few limitations, *i.e.* the calibration sample and the sample of interest should be of the same doping type and assumed to get the same thickness of the oxide layer. It is worth mentioning that this method is sensitive to parasitic capacitances between the SMM probe and the sample. To reduce the corresponding error, the samples have been placed around the same height. The "must" would be the use of shielded SMM tips.

SMM dopant concentration calibration using dC/dV method involving the measurement of the derivative of the capacitance *C* with applied voltage *V* works quite well on doped GaAs multilayers with the same type of doping. However, the comparison of dC/dV measurements between a p-doped GaAs and n-doped GaAs does not work, because the DC bias voltage applied to the SMM tip has an impact on the dC/dV electrical measurement and leads to different values according to the type of dopant.

For GaN multilayer samples, the edge areas of p-doped GaN samples are not flat and present a high roughness compared with that of the n-doped GaN samples. The edge boundary is very accidental. Different AFM probes have been broken during scanning on the edge area of interest and sometimes the AFM probe suffers various modifications of its apex radius. It is worth noting that the cleavage with sapphire substrates is very difficult. A better cleavage can help to have more flat surfaces and to distinguish each doped GaN layer.

#### • SMM measurements of doping concentration on single pure n-doped and p-doped GaAs NWs

For p-doped GaAs NWs, the mSOL calibration method has been successfully applied to measuring the dopant concentration assuming that the thickness of GaAs oxide on p-doped GaAs multilayer and on top surface of GaAs NW have the same value. Concentration values of  $(5.8 \pm 1.2) \cdot 10^{18}$  cm<sup>-3</sup> and  $(4.8 \pm 0.8) \cdot 10^{18}$  cm<sup>-3</sup> were found in the same order of magnitude as the expected values of  $3.3 \cdot 10^{18}$  cm<sup>-3</sup> and  $1.8 \cdot 10^{18}$  cm<sup>-3</sup>, respectively. On the other hand, dC/dV measurements on p-doped GaAs NWs do not show electrical contrast, which is opposite to SMM observations applying the mSOL method. Additional calibration procedure using dC/dV method needs to be investigated using new SMM tips in order to explain it.



For n-doped GaAs NWs, SMM measurements on NWs bare and covered by AlGaAs layer (10 nm) showed small electrical contrast between signals measured on the top of NWs and those measured on the insulating matrix surface. This opens the pathway to perform future quantitative measurements of doping concentration by SMM using the mSOL and dC/dV methods.

#### • SMM measurements of doping concentration on individual Si and Ge doped NWs

Doped Si and Ge NWs with different morphologies have been explored by SMM to perform dopant concentration measurements using the mSOL and dC/dV methods. NWs completely embedded have not been detected by SMM. To explain this phenomenon, information is required on the electrical properties of the substrate where these NWs have been grown on and an estimate of the thickness of the PMMA matrix. This could explain the absence of electrical contrast. On the other hand, Si and Ge NWs partially embedded show different electrical contrasts of signals measured at the top of NWs and the insulating matrix surface. These qualitative SMM explorations need to use a reference doped multilayer sample based on Si or Ge to perform future quantitative measurements on these samples.

#### • SMM measurements of doping concentration on individual NW junctions

Qualitative measurements performed on p-n junction GaAs NW samples provided by CNRS-INL have shown different electrical contrasts between the top of the GaAs NW (p-type) and the BCB matrix. The GaAs NW vertically embedded in a BCB matrix does not allow imaging of the n-doped region of GaAs NW. This first experiment suggests that a p-n junction GaAs NW placed horizontally on a highly (p or n) doped Si or GaAs substrate will be interesting for future dC/dV measurements, because in addition it will be possible to distinguish the type of doping (p or n). SMM measurements have also been performed on p-n junction GaN NW samples provided by TUBS. Unfortunately, these samples were not found appropriate for SMM imaging. These GaN NWs need to be reduced in height and the n region should not be buried in order to distinguish different electrical contrasts between p and n regions.

#### • CL and EBIC measurements

CNRS-C2N has measured by EBIC the localisation of the p-n junction to establish a first peak position dispersion, which is estimated between 0  $\mu$ m and up to 0.7  $\mu$ m from the NW top. The extension of the junction has been estimated between 90 nm and 130 nm. Using an electrostatic model, the dopant concentration into GaN NWs with p-n junction has been quantified to be in the 5·10<sup>18</sup> cm<sup>-3</sup> range for the electrons and close to 3·10<sup>18</sup> cm<sup>-3</sup> for holes. CNRS-C2N has also developed a CL protocol to quantify the dopant concentration in GaAs NWs. This method is actually extended to doped GaN NWs.

#### • PL and contactless CV

Aalto has carried out high throughput high-resolution photoluminescence (PL) imaging to characterise electrical surface passivation quality of the Si NW samples. The measurements demonstrate that surface passivation via an ALD Al<sub>2</sub>O<sub>3</sub> thin film is very homogeneous in all samples. The NW dimensions have no impact on surface passivation, as expected, since ALD Al<sub>2</sub>O<sub>3</sub> coats the NWs conformally. Also doping type of the NWs had no practical impact on the efficiency of surface passivation. Higher carrier lifetime was observed in NW samples with higher surface doping concentration due to stronger field effect generated by the dopants. Aalto also characterised the NW passivation layer properties by contactless CV measurements performed on reference NW samples that were fabricated together with the doped NW samples.

#### • Error sources and corresponding uncertainties

LNE has identified five main error sources occurring in the SMM measurements of doping concentration. They come from the error on the absolute values of the doping concentration determined by SIMS (and used to calibrate the SMM), the SMM measurement noise, the oxide layer thickness, the stray capacitances between the conic part of the SMM tip and the sample surface, and the apex radius and its possible change during the scanning. Other minor errors are due to the environmental conditions (mainly temperature) and the knowledge of the dielectric constant of GaAs doped layer and the native layer. From this analysis, LNE has established comprehensive uncertainty budgets leading to combined relative uncertainties ranging from 10% to 35% for doping concentration values between 10<sup>15</sup> cm<sup>-3</sup> and 10<sup>19</sup> cm<sup>-3</sup>.

CNRS has shown that the quantification of the errors and uncertainties coming from the EBIC are merged with the ones coming from the epitaxial growth of the NWs which follows the self-assembled growth mode leading to a dimensional dispersion of the nanostructures. In addition, it has been found that errors and uncertainties in CL currently limit the usefulness of the method for low n-type doping.



#### • Summary

This other challenging objective 2.2 was to measure the doping concentration values with the SMM scanning the top surface of NWs in contact mode with an expected uncertainty below 10 % and to compare to values determined by CL and EBIC on similar NWs. To this end, SMM calibration methods were investigated, relying on fit for purpose 2D reference doped multilayer samples fabricated by partners. Lot of measurements were performed on various pure doped NWs and NW junction samples fabricated within the project and include not only SMM, CL and EBIC techniques but also PL and contactless CV techniques. The key result is the completion of the traceable measurements of doping concentration performed for the first time on the top surface of the vertical pure doped NWs by SMM techniques. Dopant concentration values were found in the same order of magnitude as the expected values. Comprehensive uncertainty budgets have been established leading to combined relative uncertainties ranging from 10% to 35% for doping concentration values between 10<sup>15</sup> cm<sup>-3</sup> and 10<sup>19</sup> cm<sup>-3</sup>. Error sources and uncertainties were also investigated in CL and EBIC measurements.

Therefore, the overall objective was partially met, since the doping concentration couldn't be enhanced to 10<sup>20</sup> atoms/cm<sup>3</sup>, and no dataset of photovoltaic parameters was finally obtained.

#### Objective 3

To develop and validate traceable measurement methods and models for high throughput nanomechanical characterisation of NW devices, and electromechanical energy harvesters taking into account local bending and compression of NWs including the development of a traceable MEMS-SPM (< 10 pm depth resolution) for fast simultaneous nanomechanical and electrical measurement of semiconductor and polymer piezoelectric NWs.

Within the field of nanomechanical and nanoelectrical measurements of nanostructured materials including NWs, there exist typically two approaches, i.e. AFM-based nanoelectromechanical measurements and nanoindentation techniques. The former feature usually high force and depth sensitivity but limited vertical measurement range because of limited probing force. Furthermore, the measurement uncertainty of AFM-based approaches suffer, to a large extent, from the poor modelled tip area function of AFM tip in use. The latter demonstrate usually high indentation force (up to 10 mN) and larger indentation depth (e.g. up to several micrometers) with relatively low force sensitivity. Within the frame of this project, significant achievements including Berkovich-like AFM tips for material testing, conductive MEMS-SPM head, high-speed microprobes and novel microshakers have been made to (1) bridge the metrological gap between AFM nanoelectromechanical methods and nanoindentation techniques, and (2) address the critical issues relating to contact-based material testing approaches.

#### • Berkovich-like AFM tips for material testing

Typical AFM probes have conical tips featuring high lateral resolution, however they are generally fragile, especially for material testing with high probing force. Therefore, with the help of focus ion beam (FIB) facilities, PTB and TCD have fabricated Berkovich tips directly on AFM probes. The geometry of these new AFM tips coincides well with those Berkovich indenters defined by ISO 14577. The tip area function of these nearly flat AFM tips can therefore be well described by the ISO-compatible model, and the indentation measurement data can also be quantitatively evaluated using the well-known Oliver-Pharr model, yielding reliable nanomechanical measurement results. In addition, the diamond AFM Berkovich tips fabricated by TCD will demonstrate long-term stability, even for measurements of hard semiconductor materials such as GaN.

TCD will continue to develop their molding approach for fabrication of Berkovich diamond tips and thereafter plans to transfer it to free-standing AFM cantilever beams.





(a) Silicon Berkovich AFM tip fabricated by PTB

(b) Diamond Berkovich AFM tip fabricated by TCD (c) Moulded diamond Berkovich tip from TCD (d) 3D-printed AFM probe from GET/QDM

Figure 3.1 Different innovative AFM probe tips produced for nanoelectromechanical measurements

#### • Conductive MEMS-SPM

On basis of the fundamental electrostatic comb-drives, a new silicon MEMS-SPM has been designed, fabricated and two prototypes were produced by PTB. The prototypes can now generate a maximum indentation force greater than 10 mN with a maximum indentation depth up to 10  $\mu$ m. The new-designed AFM cantilever holder integrated within the MEMS allows stronger AFM probes with a cantilever beam width up to 50  $\mu$ m to be used for material testing. A depth resolution of 7 pm can be achieved, if commercial capacitance to digital converters (CDC) like AD7745/46/47 are used for displacement measurement.

Dynamic characterisation of the MEMS-SPM head using a home-developed fiber interferometer has revealed that the resonance frequency of the MEMS amounts to about 11 kHz, indicating that the prototypes can be well utilised for high-throughput areal measurements.



(a) the two prototypes fabricated (b) a diamond AFM tip clamped in the new holder

#### Figure 3.2 The two new MEMS-SPM head prototypes for nanomaterial testing

PTB has also developed a new capacitive readout circuit with high-bandwidth for the grounded MEMS-SPM head. First measurements show that the new electronics has a noise floor of about 10 pm/sqrt(Hz) even for a bandwidth up to 1 kHz. PTB together with LNE and CNRS have also developed a transimpedance based through-tip current measurement system. Using a series of reference resistors with a nominal tolerance up to 5%, the electrical properties of the MEMS have been characterised. First measurement results have proven that the electronics and MEMS-SPM head have a noise floor of 50 fA.

LNE with the technical support of CSI has designed the mechanical interface for integrating the MEMS-SPM head into their Resiscope. On basis of a slightly modified electronics with an analog interface, DFM has successfully integrated the MEMS-SPM head with their commercial AFM Park NX20 for material testing. First results have been summarised into a manuscript, which will be submitted to the peer-reviewed journal Nanoscale.

#### • Nanoelectrical measurements of freestanding GaN pillars using the MEMS-SPM head

The measurement capability of the MEMS-SPM has been investigated using a series of reference artefacts including a step height standard and EFM testing structures. Furthermore, the MEMS-SPM head has also been utilised to characterise the electrical properties of GaN pillars fabricated by TUBS. In the case of conductive diamond AFM tip used for electrical measurement, measurement results indicate that a steady-state through-tip current can only be achieved, when the probing force  $F_p$  becomes larger than 10  $\mu$ N (s. Fig. 3.1.b). Under the condition of  $F_p = 20 \,\mu$ N, the relationship between the through-tip current and the bias voltage  $V_B$  has been acquired.

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(a) SEM image of free-standing GaN micro-pillars



(b) Relationship between the probing force and through-tip current on a GaN micro-pillar.



(c) Comparison between the through-tip current along GaN nanowires and that on the substrate.

Figure 3.1 Test of innovative AFM probe tips for nanoelectromechanical measurements

First measurement results indicate that the through-tip current will appear evidently, only when  $V_B$  is increased to be larger than 5 V. These characterisation results coincide well with the bulk measurement results by TUBS.

#### • High-speed CR-microprobes

A new high-speed microprobe based contact resonance imaging system with a bandwidth up to 100 kHz has been developed by TUBS. Both the topography and the mechanical properties of NWs can be acquired during the high-speed surface scanning. First measurements on Si<111>, Cu and ZnO NW arrays have proven that this new measurement system allows for fast mechanical-performance measurements of large-scale vertically-aligned NWAs without releasing them from their substrates. The measured geometrical parameters of NWs including diameter and pitch coincide well with the values determined by scanning electron microscopy (SEM). Tip wear of microprobes including AFM probes have been experimentally investigated. DFM has written a Good Practice Guide on the "Characterisation of probe wear in AFM based topography and nanomechanical and surface deformation measurements".

#### Modelling of high-speed areal nanomechanical measurement methods including big data analysis

CMI used a mass-spring model assuming a probe with a CR frequency in the range of hundreds of kHz for describing the tip-to-wire contact. A strong effect at the top edges of the microwire was observed leading to a decrease of the CR frequency there. Both, the numerical method and experimental CR imaging illustrate that the impact of topography can be much larger than the impact of local mechanical properties. CMI had developed two toolchains for interpretation of CR measurements on TUBS samples, one based on FEM and one based on mass-spring model, with complementary speed accuracy and flexibility. Validation of these computational tools was performed on experimental data provided by TUBS and evaluated at CMI.

#### Novel microshaker to measure the averaged properties of NWs

The new piezoelectric measurement tool with a bandwidth up to 1 kHz has been designed and prototyped by ELECTRO, is in version 5 as of December 2023 and being commercially reviewed for industrial manufacture. The tool has been calibrated against standard reference quartz and LNO as well as being metrologically calibrated using traceable methods for charge and force. Force is derived from a NIST mass and local 'g'. Charge is derived from NPL calibrated capacitor and calibrated instrumentation. Version 4 of the tool has been used to measure all samples from project partners revealing typically low piezoelectric responses, but importantly non-zero values. These data are integrated with the nanoscale datasets and are being published in peer reviewed papers and conferences. The system was presented at the UK conference Piezo2023 in Glasgow, November 2023

#### • Summary

To sum up, the objective (traceable measurement methods and models for high throughput nanomechanical characterisation of NW devices) has been achieved by means of (1) successful development of traceable MEMS-SPM with a depth resolution of 10 pm and a maximum indentation force higher than 10 mN to bridge the metrological gap among currently available nanomechanical measurement approaches, (2) realisation of high-speed CR microprobe measurement system for fast areal topography and mechanical measurement of NWs, (3) modelling and compensation of tip-NW interaction during the high-speed scanning, (4) development



of ISO-compatible innovative AFM probe tips for materials testing, (5) development of innovative micro-shaker to characterise the properties of piezoelectric NW energy harvesting samples/ chips and devices. The outcomes of the above activities will promote not only the progress of metrology within the field of nanoelectromechanical measurements of NWs, but also reliable development of innovative NWs for energy harvesting.

#### Objective 4

To develop and validate traceable measurement techniques for thermoelectrical characterisation, based on fast areal thermal imaging, of NWs (thermal conductivity lower than 10 W/(mK) with an uncertainty < 10 %) under different scanning speeds and tip-surface contact.

In the area of thermophysical measurements, the main project achievements can be divided into three groups: single probe, multi-probe and non-contact measurements.

#### • Traceable measurement of NWs using single probe SThM

First of all, the consortium adapted Scanning Thermal Microscopy (SThM) in its standard configuration (single probe, ambient conditions, compatibility to commercial Scanning Probe Microscopes) for measurements on nanowires and related samples. Bulk samples based traceability chain, related to traceable measurements of sample thermal diffusivity using laser flash method, specific heat by differential scanning calorimetry, and the density by the Archimedean method, was introduced by LNE to SThM measurements on nanowires.

Together with developed SThM probe calibration methodology, the method can reach thermal conductivity uncertainty below 10% for nanowires with low thermal conductivity (see an example of the fitted calibration curve in Fig 4.1). To reach such accuracy, it is important to keep strictly steady-state environmental conditions, minimising the roughness of both calibration and studied materials and ensuring that measurement condition is the same between calibration and measurement (e.g. that we are in diffusive heat transfer regime in both cases).

A potential lack of knowledge of the heat transfer mechanism in the sample and surface roughness belong among the most important uncertainty sources. In terms of data sampling methodology, use of Force Volume measurements was found to be most promising when dealing with free standing silicon nanowires and CMI was both performing measurements in this regime and developing the data evaluation methods for this type of data within an open source software Gwyddion on which development is participating. Force Volume allows to get a thermal reference value far from the sample at every sample location, features better control over the contact formation and due to absence of lateral movement is able to work with very fragile samples.

All the above methodologies were tested by CMI and LNE on nanowire samples provided by INRIM, TUBS and CNRS. To be able to measure thermoelectric properties, it is useful to have the SThM tip galvanically separated from rest of the circuitry: for these purposes a novel transformer bridge electronics was developed by PWR and GUM, based on an inductive arm bridge with two input transformer branches and a differential branch with third transformer. PWR had also developed special nanowire mounting platforms to reduce impact of substrate in single probe SThM measurements, nevertheless, the heat flow paths in a single probe SThM can be fully estimated only via numerical simulations.





Fig. 4.1.: Thermal conductivity calibration curve example

#### • Traceable measurement of thermal properties of NWs using multi-probe technology

To address better the heat flow in individual nanowires, two **multi-probe methods** were developed. MEMS platforms developed by UAB and applied to INRIM nanowires samples represent the most elaborated devices for individual nanowires analysis developed in the project. Microfabricated suspended structures can be used to individually heat a nanowire at particular locations along its length and to measure its temperature on other locations, up to four point configuration.

The MEMS platform is designed to minimise all the parasitic heat paths: measurements are performed in vacuum and the nanowire is suspended only by the thin metallic beams, minimising thermal losses to the surrounding silicon frame. The beams can act both as a heat source or as a thermometer. The principle of thermal conductance measurement relies on precise measurement of changes in resistance of metallic beams, and consequently, the mean temperature of the beams, while applying controlled power to heat other beams. In a specific scenario where a nanowire sample with low thermal conductance (few nW/K) is loaded into the measuring structure using nanomanipulators and FIB for bonding, when one of the beams is heated to a few Kelvin, the remaining beams experience a temperature rise ranging from a few hundred millikelvin (the closer beams) to a few tens of millikelvin (the most distant beams).

On the electrical side, the measurement approach considers the use of AC signatures to take profit of lock-in strategies to enhance the measurements sensitivity. The measurements are taken feeding with oscillating currents at frequencies over 600 Hz, since characteristic thermal response of the microbeams is around 10 Hz, and therefore the temperature oscillation of the beams in negligible and the measurement resembles the DC approach. These uncoupling of thermal and electrical response of the beams is crucial for the enhanced sensitivity. With chosen electric circuitry and measurement methodology, it is possible, even with current values of a few µA, to obtain temperature resolutions better than 10 mK, close to the Johnson limit for the sensor. To ensure thermal stability, measuring chips are loaded into a closed-cycle Helium cryostat. An important part of the developed methodology was the nanowires manipulation protocol, for which a micromanipulator inside a Scanning Electron Microscope was used. An example of the micromanipulation process is shown in Fig. 4.2.

Considering that the average diameter of the NWs between beam 2 and 3 is 250 nm on average and the length 5,4 µm the thermal conductivity can be extracted,  $\kappa = (6,1 \pm 0,6)$  W/mK. This value is slightly larger than the one previously obtained on uncoated porous Si NWs grown with the same methodology, i.e.  $\kappa \sim 2$  W/mK for 250 nm NWs. The difference may be attributed to the ultrathin ZnO layer grown by ALD. The uncertainty of the thermal conductivity is shared between the measurement of the thermal conductance and the uncertainty associated to the dimensions of the NW, given the fact that the diameter is slightly different at both ends and that the outer diameter is difficult to estimate with high precision due to the intrinsic porosity of the nanowire. More statistics and averaging in the measurement of beam conductance and resolution of the thermal circuit through the complete set of equations can reduce the uncertainty well below 10%.



In contrast to SThM, the data interpretation is more straightforward, and the obtained thermal conductivity is not dependent on choice of some numerical model.



Fig. 4.2.: Nanowire micromanipulation to be placed on a MEMS platform

#### Innovative multi-probe SThM

To develop a higher throughput method capable of performing multi-probe measurements, CMI had adapted a standard commercial SThM for a dual probe operation (see Fig. 4.3). Goal of this two-probe Scanning Thermal Microscopy experiment was to use a commercially available Scanning Probe Microscope and modified commercially available thermal probes to determine thermal conductivity of an individual nanowire, minimizing the impact of heat flux towards the substrate. The probes were modified by cutting commercial sensors from Kelvin Nanotechnology (sold by Bruker). Again, use of Force Volume regime for all the measurements was necessary to prevent movement of the nanowires across the surface, similarly to single probe SThM, which allowed even probe-on-probe measurements, that were used to set a zero distance value, benefiting from the microscope positioning system accuracy in further measurements. Numerical analysis of the temperature decay curves led to values comparable to MEMS platform results, however with higher uncertainty. As a follow-up plan, a vacuum version was designed to be less affected by air heat conduction.



Fig. 4.3.: Dual probe SThM operation on a nanowire: overall image and thermal signal from one probe showing the second probe acting as a heat sink.



#### Traceable noncontact method for measurement of thermal properties of individual NWs

To address the temperature variations on larger scale devices formed by nanowires, a traceable **thermoreflectance** setup has been developed by CMI, tested on CNRS solar cell samples. Traceability is provided using platinum sensors in a heater stage located below the sample, which is used for in-situ calibration of the thermoreflectance coefficient. Multiple illumination setup, featuring a set of LED sources in the range of 375-780 nm is used to get optimum signal from different materials. Combination of measurement at wavelength where the thermoreflectance coefficient is high and where it is low is used to reduce the uncertainty related to sample bending and drift, as shown in Fig. 4.4. Multiple CCD images are used to increase the bit depth, which is further combined with lock-in detection. The biggest uncertainty is related to small sample drifts when the local thermoreflectance coefficient is determined. This was further reduced by data postprocessing in Gwyddion open source software. The setup was compared to SThM and to infrared microscopy, which is illustrated in Fig. 4.4.



Fig. 4.4.: (left) thermoreflectance response of a heated silicon probe at two different illumination wavelengths, (right) the detected drifts on a nanostructured sample during the periodic heating.

#### • Summary

To summarise, the objective (i.e. thermal conductivity lower than 10 W/(mK) with a target uncertainty of 10 %) was fully reached by two methods (single probe SThM, MEMS device) and a wider set of thermophysical characterisation methods was improved for better compatibility to nanowire samples in terms of instrumentation, measurements capabilities, traceability, throughput and uncertainty analysis.

## 5 Impact

To promote the uptake of project results and to share insights generated throughout the project, results have been shared broadly with scientific and industrial end-users. 25 papers reporting project results have been published in open access peer-reviewed international journals or proceedings, another has been accepted and is awaiting publication, five have been submitted and two more have been drafted. In addition, an article was published in Metrology and Hallmarking, the Bulletin of the Central Office of Measures, 6 Bachelor and one Master thesis have been published as a result of the project. 51 presentations have been given at conferences and the project was presented to over 100 participants at two plenary sessions of NanoMaterials for Energy Applications. A stakeholder workshop was held at the 21<sup>st</sup> Annual Metrology Congress CIM2021 in September 2021 in Lyon, France and stakeholder meetings were offered online in February and November 2022 as well as July 2023. The project has been presented at national and international standardisation committees and posted regularly on social media through Instagram, Facebook and LinkedIn. A <u>website</u> containing all social media posts has been set up and is periodically updated, in parallel to the official project site, for a wider public. 19 training events were held in the form of workshops, online webinars, staff exchanges.

#### Impact on industrial and other user communities

New contact-based measurement modes will enable industry to simultaneously measure dimensions, electrical, thermal and mechanical properties of surfaces such as elasticity, stress, adhesion and thickness of nanomaterials. Conductive AFM and SMM techniques combined with EBIC and CL techniques have the strong potential to describe overall performance, unwanted loss mechanisms, optimal operating frequencies and aging within one device. Together, these techniques will certainly fit the need of upcoming industrial production.



Advanced diamond probe technology will provide the robustness and longevity currently lacking from contact sensors today.

Industrial users have been contacted and relative key persons have joined the Stakeholder committee. Additionally, ELECTRO has developed their new piezoelectrical measurement tool which is now under commercial reviewing for industrial manufacture. ELECTRO has patented parts associated with it. The application of the new high-speed CR setup on NW arrays developed within this project for commercially available products (e. g., KlettWelding, KlettSintering and ZnO/Si solar cell on glass) has also been assessed and explored.

#### Impact on the metrology and scientific communities

Partners continued to interact with various scientific, metrological and industrial networks in order to disseminate project results. Three newly established European Metrology Networks (EMN) networks have also been contacted through the project representatives in these communities: Quantum Technologies, Advanced Manufacturing and Clean Energy Networks.

Experiences with advanced NW fabrication methods were documented in a "Report on the fabrication of NW array artefacts for demonstration of traceable measurement methods for high throughput nanodimensional characterisation of NW energy harvesters (> 10<sup>8</sup> NWs/cm<sup>2</sup>) including 3D form". First results have been presented by INRIM to VAMAS TWA2 Surface analysis in September 2021 and EURAMET TC Length in October 2021. This report was also presented at NanoWire Week in April 2022, to more than 200 attendees, and MNE2022 in September 2022 to more than 100 attendees A set of process parameters for cryogenic etching of silicon NWs established at TUBS has been transferred to INRIM to accelerate the introducing procedure of their new Oxford cryo etcher.

Experiences of NW fabrication were exploited with MBE-grown highly boron- and phosphorus-doped silicon for diffusion experiments in NWs of 300-1200 nm in diameter at WWU Münster. Furthermore, for Li-ion-battery applications silicon wires of large height (up to 15  $\mu$ m) and aspect ratio (up to 22) were fabricated. Detailed results have been published in a paper and were presented at the Physical Colloquium, TU Kaiserslautern, in April 2022, and at the conference Sensoren und Messsysteme in May 2022, to more than 100 attendees.

Training courses for members of the consortium and external audience on nanomanipulation and positioning of single nanowires on MEMS structures were held in August 2021 and March/May/September 2022. Measurement and training services/courses on nanodimensional characterisation of NW arrays using scatterometry were organised.

A one-to-one training for the consortium has been held in September 2021 at DFM, with the aim to demonstrate/investigate the in-situ performance of the MEMS-SPM head with integrated readout electronics developed by PTB, and to integrate the MEMS-SPM head into the commercial AFM (NEX20, Park) at DFM. Furthermore, one-to-one trainings within the consortium have been held on topics of NW fabrication and MEMS-SPM for material testing in July and October 2022, respectively.

#### Impact on relevant standards

The metrological outputs of this project in the fields of NW solar cells have been presented to standardisation committees e.g. IEC TC 113 'Nanotechnology for electrotechnical products and systems' and IEC TC 82 "Solar photovoltaic energy systems" to foster the creation of new standards. Good Practice Guides developed were disseminated to ISO TC 164 "Mechanical testing of metals", and the German VDI/VDE-GMA Technical Committee 3.41 "Surface Measurement Technology in the Micro- and Nanometer range" aiming to standardise the new measurement modes.

The project was presented at the IEC TC113 WG13 "Wafer-scale system integration" meeting in November 2021. IEC TC113 WG11 "Nano-enabled energy storage" has recommended the establishment of one Preliminary Work Item (PWI) on "Metrology for nanowire energy harvesting devices".

#### Longer-term economic, social and environmental impacts

The metrology developed within the framework of this project will contribute to quality control of newly developed devices for energy harvesting and storage, and consequently help to promote and accelerate the development and fabrication and enable new nanotechnologies for renewable energy industry. This will strengthen Europe's response to human-induced climate change.

The high throughput metrology for quality control of innovative energy harvesting and storage devices will substantially improve the competitiveness of the European semiconductor and small energy industries. The



developed high throughput SPM techniques can also be applied for ultrafast quality control of ultra-precision workpieces, therefore enhancing the competitiveness of European manufacturing industry.

# 6 List of publications

- 1. David Necas and Petr Klapetek, "Synthetic Data in Quantitative Scanning Probe Microscopy", Nanomaterials 2021, 11(7), 1746. <u>https://doi.org/10.3390/nano11071746</u>
- Hung-Ling Chen et al., "Quantitative Assessment of Carrier Density by Cathodoluminescence. I. GaAs Thin Films and Modeling", Phys. Rev. Applied 2021, 15, 024006. <u>https://arxiv.org/abs/1909.05598</u>
- Hung-Ling Chen et al., "Quantitative Assessment of Carrier Density by Cathodoluminescence. II. GaAs Nanowires", Phys. Rev. Applied 2021, 15, 024007. <u>https://arxiv.org/abs/1909.05602</u>
- Andika Pandu Nugroho, et al., "Vertically aligned n-type silicon nanowire array as a free-standing anode for lithium-ion batteries", Nanomaterials 11 (2021) 3137 (13pp); <u>https://doi.org/10.3390/nano11113137</u>
- Andam Deatama Refino, et al., "Versatilely tuned vertical silicon nanowire arrays by cryogenic reactive ion etching as a lithium-ion battery anode", Scientific Reports 11 (2021) 19779 (15pp); <u>https://doi.org/10.1038/s41598-021-99173-4</u>
- Capucine Tong, et al., "Cathodoluminescence mapping of electron concentration in MBE-grown GaAs:Te nanowires", Nanotechnology 22 185704 (2022); <u>https://hal.archives-ouvertes.fr/hal-03539939</u>
- Noelle Gogneau, et al., "Electromechanical conversion efficiency of GaN NWs: critical influence of the NW stiffness, the Schottky nano-contact and the surface charge effects", Nanoscale 14, 4965-4976 (2022); <u>https://doi.org/10.1039/d1nr07863a</u>
- H. M. Ayedh *et al.*, "Fast Wafer-Level Characterization of Silicon Photodetectors by Photoluminescence Imaging," *IEEE Transactions on Electron Devices*, vol. 69, no. 5, pp. 2449-2456, (2022),<u>https://doi.org/10.1109/TED.2022.3159497</u>
- M. Yin, Evaluation of contact resonance measurement data with neural networks: Master thesis. Braunschweig: Institut f
  ür Halbleitertechnik, TU Braunschweig (2022); <a href="https://leopard.tu-braunschweig.de/receive/dbbs\_mods\_00071570">https://leopard.tu-braunschweig.de/receive/dbbs\_mods\_00071570</a>
- X. Liu, et al., "Perspectives on Black Silicon in Semiconductor Manufacturing: Experimental Comparison of Plasma Etching, MACE, and Fs-Laser Etching," *IEEE Transactions on Semiconductor Manufacturing*, vol. 35, no. 3, pp. 504-510, Aug. 2022, <u>https://doi.org/10.1109/TSM.2022.3190630</u>
- 11. M. Fahrbach, et al., "Damped Cantilever Microprobes for High-Speed Contact Metrology with 3D Surface Topography." *Sensors* 2023, *23*, 2003, (2023). <u>https://doi.org/10.3390/s23042003</u>
- X. Liu, et al., "Millisecond-Level Minority Carrier Lifetime in Femtosecond Laser-Textured Black Silicon," IEEE Photonics Technology Letters, vol. 34, no. 16, pp. 870-873, 15 Aug.15, 2022, doi: <u>10.1109/LPT.2022.3190270</u>
- K. Chen et al., "Excellent Responsivity and Low Dark Current Obtained With Metal-Assisted Chemical Etched Si Photodiode," in IEEE Sensors Journal, vol. 23, no. 7, pp. 6750-6756, 1 April1, 2023, <u>10.1109/JSEN.2023.3246505</u>
- 14. O. E. Setälä, et al., "Boron-Implanted Black Silicon Photodiode with Close-to-Ideal Responsivity from 200 to 1000 nm,"ACS Photonics 2023 10 (6), 1735-1741, <u>10.1021/acsphotonics.2c01984</u>
- 15. M. Garín, et al., "Black Ultra-Thin Crystalline Silicon Wafers Reach the 4n2 Absorption Limit–Application to IBC Solar Cells," Small, 19: 2302250. <u>https://doi.org/10.1002/smll.202302250</u>
- D. Li, et al., "Linear extrapolation method based on multiple equiproportional models for thermal performance prediction of ultra-large array," Opt. Express 31, 15118-15130 (2023). <u>https://doi.org/10.1364/OE.486394</u>



- 17. T. H. Fung et al., "Efficient surface passivation of germanium nanostructures with 1% reflectance," 2023 Nanotechnology 34 355201, <u>https://iopscience.iop.org/article/10.1088/1361-6528/acd25b</u>
- N. Fleurence, et al., "Quantitative Measurement of Thermal Conductivity by SThM Technique: Measurements, Calibration Protocols and Uncertainty Evaluation," Nanomaterials 2023, 13, 2424. <u>https://doi.org/10.3390/nano13172424</u>
- 19. B. Pruchnik, et al., "Four-Point Measurement Setup for Correlative Microscopy of Nanowires," Nanomaterials 2023, 13, 2451. <u>https://doi.org/10.3390/nano13172451</u>
- 20. I. De Carlo, et al., "Electrical and Thermal Conductivities of Single CuxO Nanowires," Nanomaterials 2023, 13, 2822. <u>https://doi.org/10.3390/nano13212822</u>
- Adhitama, E. et al (2023) 'On the direct correlation between the copper current collector surface area and 'dead Li' formation in zero-excess Li metal batteries', Journal of Materials Chemistry A, 11(14) p. 7724-7734. <u>https://doi.org/10.1039/d3ta00097d</u>
- 22. Refino, A.D et al (2023) 'Impact of exposing lithium metal to monocrystalline vertical silicon nanowires for lithium-ion microbatteries', Communications Materials, 4(1). <u>https://doi.org/10.1038/s43246-023-00385-0</u>
- 23. Siaudinyte, L. et al (2023) 'Hybrid metrology for nanometric energy harvesting devices', Measurement Science and Technology, 34(9) p. 094008. <u>https://doi.org/10.1088/1361-6501/acdf08</u>
- 24. K. Chen, et al., "Harnessing Carrier Multiplication in Silicon Solar Cells Using UV Photons," in *IEEE Photonics Technology Letters*, vol. 33, no. 24, pp. 1415-1418, 15 Dec.15, 2021, <u>https://ac-ris.aalto.fi/ws/portal/files/portal/76825952/Harnessing\_carrier\_multiplication\_IEEE.pdf</u>
- 25. B. Radfar, et al., "Optoelectronic properties of black silicon fabricated by femtosecond laser in ambient air: exploring a large parameter space," Opt. Lett. 48, 1224-1227 (2023), <u>https://acris.aalto.fi/ws/portal/103236962/radfar\_Optoelectronic\_properties.pdf</u>

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