QUANTIHEAT FINAL REPORT

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4.1 Final publishable summary report

QUANTIHEAT was a 4 year project aiming at solving the problems of thermal metrology at nanoscales by delivering accurate and traceable metrology tools, for enabling the thermal management and advancing the development of new generation nanomaterials. A key promising technique is the Scanning Thermal Microscopy (SThM). QUANTIHEAT was centred around this technique. The need was for a comprehensive thermal measurement and modelling technology for use at the nanoscale. 21 strategic partners (***attachment1***) from European Research Institutes and Universities including nanofabrication platforms, Metrology Institutes and Industrials developing nanomaterials and processes (nanoimprint lithography resist, Atomic Layer deposition, thermoelectric and thermal interface materials) and scientific equipment gathered for this project.

During the first year, the industrial specimens and the requirements for new generations of nanomaterials and processes were defined in detail. Measurement and modeling pathways linking thermophysical measurements with industry specified materials were identified. Recommendations were made for terms and definitions currently used in the nanoscale measurement community applicable to SThM. National Metrology Institutes developed methodologies of uncertainty budget analysis. The requirements for calibration, test and scientific samples for evaluating SThM measurement were specified and test plans for experimental research to be carried out were established. On this basis, passive calibration, test and scientific samples as well as industrial samples and four categories of active devices were designed and fully characterized (***attachment2***). Characterization and modelling results were first mainly aimed at improving the first sets of test samples and refining the thermal characterization techniques to be developed and/or applied to solve critical aspects related to manufacturing processes, materials and characterization. Calibrations, design of experiments, interlaboratory comparisons and measurements were performed in accordance with the three test plans established for SThM thermal conductivity, polymer phase transition temperature and temperature measurements respectively. Idustrial nanomaterials and manufacturing processes were developed, supported by SThM characterization results. New instruments implemented during project were fully demonstrated. This include new and evolved SThM probes, new SThM-based techniques combining SThM with Scanning Electron Microscopy and Infra-Red radiometry, a SThM calibrated in a liquid environment, a thermal–force imaging mode and an industrial SThM. Supporting modeling activity provided BTE-based simulations of the thermal distributions of confined geometries heated with localized source and numerical codes for heat conduction issues in several key classes of nanomaterials were developed. Methodologies for treatment of complex tip-sample geometries were established. Fast modeling tools were developed for speedup of experimental data analysis and for more complex models.

The analysis of all measurement and simulation results enabled then the evaluation of sensitivity, spatial resolution, and ability to detect subsurface and embedded structures using SThM methods. Good practice guides for SThM measurements and the assessment of measurement uncertainties were also completed. Methods and methodology were validated on internal and external industrial samples. Fifteen key exploitable results that may be generalised in 4 categories were identified (***attachment3***): (1) new tools for SThM that includes good practice guides, passive and active samples for calibration and measurement characterization, microscopy equipments and modes, and modelling and software, (2) thermal modelling for nanomaterials, (3) new industrial nanomaterials and processes and (4) other thermal methods. For maximizing the impact of the project (***attachment4***), partners also participated in 309 dissemination actions including 73 scientific publications and proceedings.

Project context and the main objectives

QUANTIHEAT was a 4 year European large scale-NMP project (Dec. 2013 to Nov. 2017) aiming at solving the problem of thermal metrology at the nano-scale and at delivering validated standards, methods and modelling tools for nanothermal design and measurement.

CONTEXT_ The control of heat flow is central to all technologies. According to the first law of thermodynamics, heat is the universal consequence of physical activity. At the same time modern material science and technology is increasingly devoted to the control of matter on the nanoscale and miniaturisation of device elements well below 100 nm. By nanostructuring materials their physical properties may be engineered to achieve optimal performance. Examples include materials used in renewable energy generation (thermoelectrics, photovoltaics) and structural composites. Thermal control is the dominant problem in many of these fields. For example, the continuous linear scaling of clock frequency in silicon device technology has been suspended for the last ten years as a direct consequence of the decreasing element size and increasing power density in VLSI systems. This is the first aspect of Moore’s law to fail and it has failed directly because of thermal management problems at the nanoscale.

The flow of heat at the nanoscale is completely different from that experienced in macroscopic systems. The dominant phonon wavelengths at room temperature are of order a nanometer with ballistic mean-free path extending from tens of nanometres (in copper) to hundreds of nanometers in Si. Accordingly, at the nanoscale heat flow in solids ceases to be entirely diffusive and may, indeed, be quantized. Convection is suppressed. Radiative transport, where significant, takes place in the near field, since the wavelength of thermal photons is approximately 10 µm at room temperature. Accordingly, the normal methods of modelling and design used for macroscopic thermal work are completely inappropriate.

No effective tools for thermal measurement at the nanoscale currently exist. The highest spatial resolution systems which are used for quantitative thermal measurement are based on optical effects, such as IR thermal emission, Raman spectroscopy or photoreflectance. The spatial resolution of all of these methods is limited to 500 nm or greater. The key promising technique for thermal measurement at the nanoscale is Scanning Thermal Microscopy (SThM), but this remains highly non-quantitative in normal use. The need is for a complete thermal measurement and modelling technology for use at the nanoscale. The QUANTIHEAT project had been designed to deliver this.

If the outputs of QUANTIHEAT were to be useful as practical standards in the real world, it was essential that they were formulated in such a way as to promote their adoption by non-specialists in several key application areas. Accordingly, QUANTIHEAT included the following **applications**:

(1) **Thermal -nanoimprint lithography (NIL)** where materials are modified at the nanoscale by combined thermal and mechanical stresses,

(2) **Novel nanostructured microparticle and CNT-based interconnect materials** in which the thermal and electrical properties of metallized nanoparticles must be optimised, in particular for Thermal Interface Materials (TIM),

(3) **Atomic layer deposition (ALD)** where the exquisite sensitivity of thermal imaging techniques to atomic scale interfaces will prove to be a valuable tool for process development,

(4) Novel **generation of nanostructured thermoelectric materials (TE)**.

To reach its objectives QUANTIHEAT brought together a team composed of leading experts in their fields.

Consortium gathered 21 partners, from 9 different countries that are leading experts in their fields (***attachment1***): 10 academic leading groups in thermal nanoscience and nanoengineering, thermal nano-measurements and nanofabrication, and thermal nanometer-scale instrumentation, 3 National Metrology Institutes (NMIs) and 8 industrials developing materials and fabrication processes or characterization equipment.

THE KEY OBJECTIVES of the project were to:

- Establish a consistent and rigorous terminology in the vocabulary for nanoscale thermal metrology,
- Characterize existing microscale and nanoscale SThM measurement methods and traceably quantify their repeatability and reproducibility,
- Develop new metrology tools, including calibration, reference and test samples as well as modelling tools; derive test protocols for the most promising methods and push the dimensional limits of thermal metrology down to 50 nm,
- Use these validated metrology tools to characterize the physical mechanisms of micro and nanoscale energy transfer between two solid objects (probe and sample). The results had to be used to refine existing models of thermal transport at the nanoscale. The models have then to be used to acquire a new quantitative understanding of heat transfer at the scale of nano-contacts such as those operating inside nano-crystalline, nano-composite or nanoporous materials,
- Apply the newly developed tools to the design and optimization of new SThM nano-sensors, benchmark these tools and sensors in the frame of specific relevant applications involving: nano-composite and nanostructured materials.

As originally listed in the Annex I of the GA, for that, the overall scientific and technological strategy of QUANTIHEAT was divided into five main steps preceding the project result applications. To each step corresponded a R&D sub-project (SP) (***attachment5***). Each R&D SP consisted of2 goal-oriented work packages (WP). The application of new technologies was made in a final R&D work package (WP11). Technical work was supported by 2 management WPs and 1 dissemination and exploitation WP.

QUANTIHEAT was coordinated by CNRS. The scientific management was led by CNRS with the support of SP&WP leaders who compose the project executive and scientific boards. Moreover, an external advisory board, composed of 4 members from Academia and Industry, was created to provide advice and guidance to the Consortium.

Project objectives are precised in this report per SP and WP. The various interrelated links between SPs and WPs are also underlined.

SP1 "Specifications and methodology" was to provide at the end of the first year of the project the basis for the technical activity carried out within SP2–SP5. Specific goals concern the establishment of an agreed common basis for the comparison of thermal nano-measurements, having also to provide the targets to reach, and an efficient way of controlling the progress of the project.

WP1 "Materials and applications" aimed at the definition of:

- the requirements for new generations of nanomaterials of interest and for specific applications in terms of thermophysical performance, preparation, environment specifications etc. and specify the industrial application oriented specimens.
- specifications for the methodologies and characterization techniques to be used and or developed for multiscale analysis of heat transport, thermophysical and thermomechanical properties at different length scales.
- the initial measurement and modelling pathways linking thermophysical measurements with industry specified materials.

The objectives of **WP2 "Nanoscale thermal terminology and definitions, and experimental design"** were to provide:

- recommendations for terminology and definitions for SThM measurements with the intention of submitting them for standardization by the end of the project.
- the technical performance specifications for the specimens needed for the evaluation of SThM
- the outline testing plans for the modelling and experimental research to be carried out within the project.

SP2 "Samples and materials" was oriented towards the development (design, fabrication and characterization) of:
- reference samples to investigate the traceability, accuracy and precision of SThM methods and test samples for specifying the local measurement, comparing different length scales in **WP3 "Passive test and calibration samples"**,
- "real" nanoprocesses and nanomaterials for industrial applications to investigate the relevance of SThM to resolve critical aspects related to manufacturing processes and thermophysical characterisation in **WP4 "Nanomaterial development exploiting SThM".**

Reference samples to be fabricated corresponded to bulk and film materials for which length scales are larger than the mean free path of the energy carriers. Test samples were nanostructured materials having to be designed and fabricated to enable the specification of the ultra-localized measurement of SThM relevant to the applications. Samples included features such as significant dimensions less than the mean free path of the dominant thermal carriers and controlled topographic variation. Sample selection has to subsequently be extended to materials and devices where nanostructure gives rise to thermal management issues such as heat transfer in thin films of a few nanometers thick, interfaces between materials, in nanoporous materials and nanocomposite polymers among others. For these samples, devices having a stepwise increase in complexity has to be investigated. Real nanoprocesses and nanomaterials for industrial applications concerned Thermal and UV-NIL, ALD and interconnect materials brought by the Consortium industrial partners MRT, Picosun and Conpart respectively.

SP3 "Modelling" aimed at realizing a breakthrough in modelling ability not only to advance the understanding of heat transfer at the micro and nanoscales but also to provide the modelling tools for all the RTD work undertaken during QUANTIHEAT. The objectives were:
- to establish new design rules derived from length scale models for nanomaterials in **WP5 "Modelling thermal properties of materials"**,
- to develop new tools for modeling the proximal and contact thermal interaction between nanoprobes and samples in **WP6 "Probe–sample thermal interaction modelling"**.

After rational simplification these have to be integrated with existing models for probe-sample systems studied.

SP4 "Advanced techniques and tools" focused on the development of new SThM tools, probes and techniques for physical understanding of heat flow at the nanoscale and quantitative measurement of thermal properties. More specifically, the objectives of **WP7 "temperature calibration samples"** were to:

- Develop temperature reference devices and heater devices for the calibration of the SThM tip temperature and the analyse of the influence of parasitic heat paths during SThM operation,
- Provide a completed set of active heater devices for thermometry using the 3-omega method;

those of **WP8 "New thermal techniques/SThM probe and software for data processing"** were to:
- Develop new and evolved SThM probes optimized for routine quantitative thermal characterization at the nanoscale,
- Develop different new SThM- based well beyond state-of-the-art techniques combining SThM with other characterisation methods: Scanning Electronic Microscopy and Infra-Red radiometry, allowing a more in depth study of micro and nanoscale heat transfer and multiscale analysis simultaneously,
- Evaluate the performances of new thermal modes,
- Develop new software tools for real time and post-processing of SThM data.

In **SP5 "SThM evaluation"**, SThM analysis of the full array of new reference, test and industrial samples had to be performed under different experimental conditions (probe temperature, surrounding gas and pressure, force, probe/sample spacing). For each existing SThM methods and novel techniques, analyses of the experimental results had to allow:

(a) the elucidation of the relative significance of the factors contributing to the thermal interaction of tip and sample,
(b) the validation and/or improvement of the modelling of measurements, the inclusion of the effect of probe, interaction, and sample for each technique used,
(c) the estimation of spatial resolutions of thermophysical properties.
Design of experiments (DoE) and inter-laboratory comparison exercises using the different techniques measuring the same samples have to define the best calibration protocol for each technique, the sensitivity of the method to the wanted parameter (thermal property or temperature), and the uncertainty of the measurement related to the topography, surface roughness and environment. Depending on the results of these exercises, proposals have to be made concerning improvements to the samples and the protocols, the suitability of the selected samples as "reference samples" for calibration of SThM, and which of the developed calibration protocols should be adopted for standardization. The objectives of SP5 were therefore to:
in **WP9 "SThM experiments and measurements",**

- establish a data-base of the results obtained with the samples fabricated in SP2 and SP4 for each of the different SThM techniques used, allowing the study of the probe-sample thermal interaction through comparison with simulations from SP3
- provide the measurements planned by the DoE and inter-laboratory comparison exercises defined in SP1 and initiated in SP2.

in **WP10"Evaluation of SThM for thermal metrology and nanoscale thermal terminology",**

- evaluate SThM methods available and developed in the project through the analysis of partner results of DoE and inter-laboratory comparison exercises.
- provide a draft of standard for SThM calibration for the SThM measurement of (i) thermal conductivity/conductance, (ii) surface temperature and, (iii) phase change temperatures
- report on the assessment of uncertainties for thermal conductivity,thermomechanical and temperature measurements by SThM method.

Strictly at the technical level, the objective of the **WP11 "New technology application"** had to be achieved thanks to the activities of validation and demonstration of the new products. Impact on industries had to be managed through dissemination and exploitation activities that were parts of the WP12: "Dissemination and exploitation" of the project. The objectives associated to WP11 were:

- Identify the most effective new technology for calibration, material analysis, and robust and repeatable measurements of nano-thermal phenomena for prototyping and demonstration activities.
- Provide the selected prototypes. This includes passive and active reference and calibration samples, SThM probes and measurement systems from the outputs of SP2, SP4 and SP5.
- Integrate SThM probes, calibration samples and new hardware with a Commercial SPM Platform (CSI AFM).
- Demonstrate both the capability and usability of the prototype systems through measurements of samples from consortium end-users and from outside the consortium. For THALES, fabrication, preparation and characterization of thermal interface and thermoelectric material samples.
- Evaluate the thermal performance of novel conductive adhesive for microelectronics interconnect
- Report the role and prospects of SThM for the R&D nanomaterials from consortium end-users
- Present the novel instrumentation and methods implemented during the project to SPM tool manufacturers in the EU and worldwide to encourage exploitation of the intellectual property developed during the project.

The main W12 Dissemination / Exploitation objectives were to:

- Regularly update the tools required to disseminate information and results of the project within the consortium and outside the project. This includes project internal and external websites and dissemination mailing list, and the second annual e-newsletter.
- Disseminate project results through participation in conferences and workshops, scientific and technical publications in academic and trade journals, the organization of scientific events, for scientific and industrial communities at both national and international levels.
- Pursue the actions initiated and refined in collaboration with an ESIC Expert from EC for maximizing the project impact through the exploitation of the project results.

The project divided in three periods (M1-M12), (M13-M30) and (M31-M48) (***attachment6***) had to lead to 70 Deliverables (including 58 deliverables for the technical work) associated with 21 Milestones. Thus, the progress of the work had to be reported step by step and regularly checked by all the partners involved in the project.

Main S & T results/foregrounds

Scientific and technological results of the QUANTIHEAT project were obtained according to the strategy described in Annex I of the GA. The 58 deliverables related to the technical work were successfully completed. Due to the strong collaborative character of QUANTIHEAT and the numerous interrelations between its SPs and WPs (***attachment7***) this report of the main S&T results will not however be based on the structure of the project (ie. per SP or WP) but will be grouped following four main topics:

1. Nanoscale Thermal metrology using SThM and new tools for SThM
2. Thermal modelling for nanomaterials
3. Nanomaterials developed and /or characterized
4. Other thermal methods developed.

1_NANOSCALE THERMAL METROLOGY USING STHM AND NEW TOOLS FOR STHM

To address the main challenges in micro- and nanoscale thermal transport linked to scaling, QUANTIHEAT performed experiments on length scales ranging from tens of microns to sub-10 nanometers using SThM, which has the capability to address most of this range. Different microscopes at different institutions were used (commercial, home-built and newly designed) employing different probing tips, specializing on different length scales (***attachment8***), sample types and environmental conditions. Length scales in SThM were covered by varying the contact area between probing tip and sample, and raster-scanning a sample over several length scales. To obtain a full picture of nanoscale thermal transport, we applied and developed alternative thermal methods.

The scaling issue was tackled, in parallel, using custom fabricated samples. Test samples produced as part of QUANTIHEAT range from homogenous samples (isotropic in 3D), thin films, multilayers and atomic layers (isotropic in 2D), ribbon and wire structures (isotropic in 1D), to composites (0D isotropic), with structural sizes from micro- to nano- scales. We will see that the study of the samples, supported by modelling and simulation led to a rigorous definition of the relevant quantities measurable and relevant in micro- and nano- scale thermal transport in general. Reference samples were also defined, allowing any user with any method to benchmark their measurement system against a defined standard, with special attention given to surface roughness and surface chemistry of the samples, as these parameters have a strong influence on the SThM measurement.

1.1_ CHARACTERIZATION OF SThM MEASUREMENT

The characterization of the measurement of thermal conductivity, phase transition temperature of polymeric materials and temperature by SThM were the main considerations of the QUANTIHEAT project. For thermal conductivity and phase transition temperature measurement, the SThM probe is operated in active mode and the sample is passive. In temperature measurement, a passive probe is conventionally used to measure the sample that is self-heated (active sample) or externally heated. Two categories of samples, passive and active, were then studied and developed. Their technical requirements were specified by partners in WP2.

A review of literature allowed the identification, rationalisation and definition of all key terms applicable to SThM measurements as well as those to be developed within the project for standardization. These definitions and the analysis of the major sources of uncertainty in SThM obtained from the literature assisted in defining the functional specification required of the specimens to be used for the characterization of the SThM measurement. The uncertainties in SThM measurement were classified into different types and flowcharts for selected systems in order to develop a systematic method to analyze the different sources of uncertainty. Methodologies to evaluate uncertainties were formalized by the NMI partners and the identified sources of uncertainty supplied for inclusion in the Design of Experiments (DoE) and in the Interlaboratory Comparisons (IlC) for SThM measurement characterization.

SThM measurements (including calibrations, DoE and IlC exercises) of all the samples developed were performed in the frame of WP9 following the roadmap of sample characterization. The SThM characterization results were initially aimed at improving the first sets of test samples and refining the thermal characterization techniques developed. Few SThM users were in charge of the sample measurements at this stage. At M36 of the project the samples with regards to their oriented goals were priorised, identifying those to be fully characterized by the end of the project in order to reach our objectives. Modelling activities performed in SP3 allowed and supported the analysis of measurements. Samples then passed to WPs 8, 9, 10 and 11 for further investigations and prototyping activities. The main results of the measurement and analysis of these samples are reported here for both the passive and active samples.

1-1.A CHARACTERIZATION OF SThM MEASUREMENT USING DEVELOPED PASSIVE SAMPLES

Passive calibration and test samples were designed, fabricated and characterized by techniques other than SThM in WP3. The designs and process flows of passive micro and nanoscale test and reference samples and the protocols of cleaning and storage of the calibration samples were ready in June 2015. In November 2015, some fabricated samples were considered mature with their goals having been reached. Some of these "mature" samples were then duplicated and disseminated to more partners as part of WP9 for evaluation of the various SThM techniques available within the consortium. Additional samples were manufactured using other materials to validate the modelling and the interpretation of SThM measurements related to them.

Passive samples can be separated in two main categories:
- Reference samples for the study of SThM calibration for thermal conductivity or conductance and (in the instance of polymeric materials) of phase transition temperature.
- Test & reference samples for assessing SThM performance and measurement procedures and anticipating the variability of measurement conditions of practical industrial samples. These samples were also designed to analyze nanoscale heat transfer within nanostructured materials, maximizing the impact of the project**.**

1-1.A.1 Thermal conductivity measurement using thermal reference samples

Measurement principle: Thermal conductivity measurement by SThM requires the heating of the sample by the probe operated in active mode. For this reason, resistive probes are mainly used (***attachment8***). The probe is heated by the Joule effect and plays the role of thermal source in contact with the sample. Measurement is then based on monitoring probe electrical resistance (thermal-resistive probe) or thermal-voltage (thermocouple probe) and is performed in two steps: (1) with the probe at a distance d away from the sample surface and (2) with the probe in contact with the sample surface. The variation of this measurand between (1) and (2) is representative of the global thermal conductance of the probe-sample system within its environment, requiring a model of the system to determine (i) the heat flow transferred from the tip to the sample and (ii) the thermal conductivity/conductance of the sample.
Analytical modelling and numerical modelling of the probe-sample system were used/developed. Numerical modelling was developed and adapted during the project to specific probe geometry and dimensions. As a consequence, they were not immediately available in the project. Therefore, partners decided to use the phenomenological modelling in [Therm. Acta 425 69 (2005)] to ensure a common approach in analysing the measurements. The selected model is based on a description of the probe-sample system in its environment using a network of thermal conductances. The modelling parameters can be obtained through calibration using reference samples.
Here it is important to state that, since 1997, various SThM probes have been developed (some commercial). As a consequence, each user group has its own approach to calibration and data processing, employing different samples and experimental conditions. To ensure that calibration protocols are appropriate and consistently used, QUANTIHEAT undertook interlaboratory comparison exercises with dedicated material standards and reference samples developed for this purpose during the project.

Reference samples developed: Fourteen "thermal reference samples" were selected by partners. This selection made the assumption that the thermal conductivities of the calibration samples were the same at macro- and submicron-scales. As the influence of roughness was not known at this stage of the project it was agreed that the "thermal reference samples" would be prepared with the lowest roughness possible. All sets of passive test and calibration samples had also to be prepared from the same batches of material to ensure consistency. Consortium partners arranged the mechanical polishing of specimens as well as the ultramicrotomy of polymeric samples after their shaping. Protocols for cleaning samples and cleaning and calibrating the SThM sensors were also established. Extensive measurement campaign to obtain structural, mechanical, chemical, electrical, optical and thermal characteristics of the 14 samples was performed. Thermal conductivity of the samples was obtained by using an indirect method traceable to the SI. Here the calculation of the thermal conductivity from the measurements of thermal diffusivity by laser flash method, specific heat by DSC and density by Archimedean method was adapted. Thermal diffusivity and conductivity measurements of the samples by thermoreflectance, Time Domain Thermoreflectance and by electrical means were also performed. Thermal diffusivity measurements by photoreflectance microscopy for different thermal penetration depths (< 25µm) by varying the heating laser modulation frequency provided information on the sample homogeneity. Structural analysis was performed by AFM, nanointendation and SEM. The analysis of all these characterization results were fed into the selection process for samples to be used in the DoE and IlC.

Results of the SThM investigation of samples: The DoE constitutes a first analysis of a large dataset of measurements performed using SThM by the partners, and was and will be used to improve existing measurements methods/procedures. Concerning IlC, partners calibrated their systems against specified samples before starting measurements of four assigned samples for reference values of thermal conductivity where witheld. Critically, these different samples did not lead to the same measurements by the partners. The good performance of the measurement was only the case for one sample alone for which the reference value of 0.329 W.m-1.K-1 lies within the interval [0.085; 0.417]. For each of the 3 other samples, the participants measured values of thermal conductivity below the reference values. Several explanations were suggested: difficulty in identifying a suitable model for the inverse solution to compute thermal conductivity from the measurements, samples falling outside the range of sensitivity of SThM and shortcomings in the measurement protocol. Results have also confirmed that the higher the thermal conductivity of the sample, the more difficult it is to get a reliable value through the IlC exercise.

SThM measurements for the IlC showed that among the 14 samples selected there were too few with thermal conductivity lower than 60 W.m-1.K-1 for SThM calibration. Therefore, new bulk samples were purchased with low roughness. These new samples were characterized in terms of thermal conductivity, roughness and mechanical properties. All SThM users performed then new SThM measurements of these samples with a methodology they had refined.

These measurements have identified that the range of thermal conductivity sensitivity depends on the type of the probe used and that for a given type of probe it is strongly dependent of the real shape and size of probe and material at its tip apex. It has also been shown that the available SThM microprobes are mainly sensitive to thermal conductivity lower than few W.m^{-1}.K^{-1} (***attachment9***). As a result, even with a full calibration curve, there will be a high degree of uncertainty in any measurement performed on an unknown sample. This specifically concerns probes with smallest tip-sample contact area. Consequently, new approaches need to be developed if such nanoprobes are to be adapted for thermal conductivity measurement. Overall, the measurements of the thermal conductivity with nanoscale probes (e.g. KNT-probes) have shown that in the ultimate nanoscale regime the bulk thermal conductivity becomes less useful parameter. The project results show that it may be more essential to consider "thermal conductance" as a function of contact dimensions and device geometry that becomes more relevant to the nanoscale heat transport phenomena, and the future definitions in metrology. Significantly, the nanoscale KNT probe does allow distinguishing between higher thermal conductivity materials up to few 10 of Wm^{-1}K^{-1}, but would need to be coupled with an explicit model for the contact thermal resistance.

A full evaluation of the uncertainty associated with the thermal conductivity measurement by SThM was performed for the first time. A Monte Carlo method was used to perform the propagation of distributions according to the principles of the ISO/BIPM "Supplement 1 to the Guide to the expression of uncertainty in measurement". The relative standard uncertainty (k=1) on thermal conductivity measurement performed using a SThM equipped with KNT probe was estimated to be around 10 % in the most favourable configurations (low conductive materials for which the sensitivity is the highest). This quantitative data is specific to the particular operating conditions and SThM devices used. However, the methodology developed can be applied to evaluate the measurement uncertainties for other operating conditions and other SThM apparatus or probes.

Conclusions: Exercises based on the use of a set of thermal reference samples enabled the refinement of measurement and calibration protocol that is a part of the Key Exploitable Result (KER) N° 1 of QUANTIHEAT. Furthermore, collection and analysis of the data permitted evaluation of various types of SThM probes. Based on previous statements, the set of samples constitutes a prototype produced by the project and an application describing this set was made available on the project website. However the consortium decided to removed it from the project KERs. From a practical point of view for SThM users and for the exploitation of reference bulk samples, more low thermal conductivity materials would need to be included. Furthermore, the arrangement of reference materials on a single holder rather than individual samples for each reference material should be useful. Both specifications are in line with the properties of QUANTIHEAT Oxide Step Sample. Partners are currently working on these potential advantages for SThM calibration. First results from this work are given in part **1-1.A.3** of the report. Calibration based on the use of the advanced modelling developed during the project and that will be made available to project partners on an online software tool implemented at the end of the project must now be considered (refer to section 1-2 of the report).

1-1.A.2 <u>Measurement of the polymer phase change temperature using reference samples</u>

Measurement principle: In case of phase change temperature analysis, measurements can be performed on selected spots on the sample surface by following the deflection of the cantilever during fast heating of tip, while the tip remains in contact with the sample surface. These measurements are a form of thermomechanical SPM measurement. The probe mainly used in the project for these measurements was the doped Si (DS) probe (***attachment7***). The calibration procedure chosen to be tested and improved was based on that of Anasys Instruments who commercially distribute the DS probe. In this procedure the probe temperature is calibrated using three semi crystalline polymeric samples that cover the range of melting temperatures up to about 240 °C and exhibit a sharp melting transition. This allows the determination of a calibration curve giving a correlation between the probe heating voltage and the sample temperature (assumed equal with the tip temperature).

Developed reference samples: For the evaluation of this procedure and measurements based on it, a set of reference samples was developed in QUANTIHEAT. For its development different techniques for producing the calibration and test specimens for thermomechanical SPM techniques were reviewed. The production techniques required homogenous specimens. Critically the preparation techniques had to produce specimens with reproducible thermal and mechanical properties. The technique therefore selected was to microtome the cross-sectional surface of a moulded polymer rod. Microtoming the specimens ensured that the surface layer that forms during casting of the rod was removed. Microtoming also avoids damaging the specimen surface with heat that can occur when machining/milling techniques are used. The reference specimens included 5 amorphous polymers and 4 semi-crystalline specimens. They also cover the range of transition temperatures up to about 240 °C. Amorphous and semi-crystalline polymer rods were purchased and specimens were cut to the correct length and then microtomed. To produce flat defect-free surface the surface of all specimens was prepared using ultramicrotomy (cryogenic cutting depending on material). Indeed basic microtomy could not provide sample surfaces of high enough quality to enable sufficiently reproducible measurements. Glass transition and melting temperatures (as appropriate) were determined using differential scanning calirometry (DSC). Nanoindentation was also conducted on all calibration specimens. Modulus and hardness values were found not to vary across the surface of the specimens, indicating that they were homogenous at this scale.

Main results: After following the calibration and measurement procedure of Anasys Instruments, we established a first draft of a more detailed and improved measurement procedure. This allowed users to minimize thermal drift in the measurement and systematically ensure that the probe was not contaminated, operating under the same conditions. Results obtained showed that the contact force (between 7 and 50 nN) between the probe and the sample is not influential on the response of the probe for such measurements. IlC showed that melting temperature and phase transition temperature measured by mean of SThM can be compared with the reference values and their trend is similar. However there were not enough participants to apply the standard ISO 5725-2, determination of repeatability and reproducibility. A systematic difference was obtained between the results of some partners (***attachment10***). This can be attributed to the lack of accuracy of the calibration procedure used. While a quadratic fitting curve is employed with the three reference samples used for calibration as advised by Anasys Instruments, such fit is not suitable for measurements on more reference samples as found in QUANTIHEAT. This has demonstrated the main limitation of the T_m and T_g measurement method. As a result, a new protocol was designed to reduce the possible uncertainty sources to a minimum by applying exactly the same procedure for temperature scale calibration and for the measurement of unknown samples. This simplifies the uncertainty budget but also affects the uncertainty of the temperature scale, which is much larger than if the probe could be calibrated as in the temperature measurements using SThM (see Sect. 1-1.B). The uncertainty on measurement was determined by using the Monte Carlo uncertainty propagation technique and it has been confirmed that the largest contribution is given by the temperature scale calibration. The uncertainty on the measurement of an unknown sample has been estimated to be of order 12 K. It is therefore crucial to follow the measurement protocol correctly, including collecting all supporting data, such as drift after feedback is switched off. It is also recommended to perform the calibration before and after the measurements to evaluate potential systematic errors related to calibration changes.

Conclusions: The work performed with the new set of reference samples enabled refinement of the measurement and calibration protocol that constitutes a part of KER N°1. It was intended for the set of selected samples to form the basis of a prototype and an application note describing this set was available on the project website. However careful evaluation of the data resulted in the decision to remove it from the project KERs as it does not provide a more advanced approach than the existing Anasys Instruments one. However the work was valuable as measurements of more samples have enabled conclusions to be drawn on the uncertainty of measurements that can be obtained with the method used.

1-1.A.3 *Characterization of SThM measurement using nanostructured test samples*

In the context of terminology and definition, an indication of the relative immaturity of our understanding of the artifacts inherent in SThM is the observation that the *definition and the experimental determination of the spatial resolution of a SThM method are not common across the field.* All too often the attribution of a feature in a thermal measurement is rendered uncertain by the simultaneous presence of a topographic feature or a difference in the surface condition. The spatial resolution in a SThM image is often estimated as being equal to the extent of the thermal contrast observed around nanostructures embedded in matrix. Is the nanoscale detected signature representative of the real thermal conductivity at the sample surface/subsurface? Would the spatial resolution not better be estimated from the real size of nanostructures constituting well-known nanostructured materials? These points were resolved through SThM measurements of nanostructured samples and simulation tools developed for this purpose during the project.

(i) Spatial resolutions of SThM probes and the impact of topography on the thermal contrast

The analysis of spatial resolutions of thermal probes and the impact of topography on the thermal contrast in SThM were performed using samples that can be classed into two groups: topography free samples and samples having well-controlled patterns with different thicknesses. A prime cause of imaging artefacts in SThM is variable tip-sample contact area when a tip encounters topography. This makes characterisation of the thermal-spatial resolution a significant challenge. Any topography free sample to be fabricated has to offer well-defined, abrupt, and high-resolution changes in thermal conductivity with nearly zero topography and roughness.

Multiple fabrication iterations with the aim of optimizing sample parameters – global flatness, pattern fidelity and minimal local topography were made during the project for a ***High Thermal Contrast*** topography free ***Sample***. Initial characterizations showed low topography (<5nm) between features. Designs and fabrication procedures were completed and circulated. Second generation designs/fabrication procedures were generated to investigate phenomena highlighted by the first samples. The samples successfully demonstrated the relationship between (topography free) feature size and SThM signal – a phenomenon that can be interpreted as resolution. Samples were circulated to several partners for evaluation with different probe types using an edge scan method. Results were obtained for KNT, Wollaston, Nanonics and thermocouple wire probes with all agreeing with the contact radius calculated and/or measured for each using alternative methods (***attachment11***). This demonstrated that this sample provides a way of characterising the true thermal spatial resolution of a SThM system, and an effective method of comparing different probes and instruments.

A powerful capability of SThM is its ability to detect sub-surface features that have contrast in thermal properties with respect to the top layers. However, the sensitivity of SThM to sub-surface features depends on the probe type and experimental conditions. This makes the interpretation of the experimental data a challenging task. A second design was investigated to characterize and estimate the in-depth spatial resolution of SThM probes. It also provided an approach for the measurement of thermal properties of thin films on substrates and analyzing the effect of topography on SThM signals and enabled photothermal techniques for comparison. The sample consists of a polished monocrystalline silicon wafer that has patterns of thermally grown SiO_2 with different thicknesses (***attachment12***). The optical and AFM characterization were performed before distribution to different partners. A clear relationship between the SiO_2 film thickness and measured thermal signal was obtained with thermoreflectance and for all SThM user partners, using all SThM probes available within the consortium. As a result, this sample has been proposed as a method of calibrating SThM probe response as a function of sample thermal resistance. This was backed up with modelling, specifically tailored to the sample. Let us add that factors like tip-sample contact resistance and tip-sample contact area can mask the true sensitivity. These factors change dynamically with wear and tear and one needs to quantify the degradation of the probe before and after scanning. The ***Oxide Steps Sample*** provides a series of surfaces made of the same material, with identical roughness, but with different effective thermal conductivities. This allows the SThM sensitivity, with a given set of operating conditions, to be measured but also through modelling to extract the contact area and contact resistance from the experimental data giving additional figures of merit of a probe before and after a scan. The thermal profile from a topographic image was reconstituted showing the mastery of probe behaviour here and now as well as the validity and relevance of the software implemented for fast SThM data analysis (refer to section 1-2).

A third design combining some features of the above high thermal contrast topography-free sample and the oxide steps sample was a topography-free sample with buried Si steps under planarized SiO_2 (***attachment13***) for characterizing the effect of probed volume and buried features in SThM measurement. These ***Buried Step*** topography free ***Samples*** were designed/fabricated in two process round iterations. Final samples had steps of width 300 nm, 600 nm, 1 micron and 2 microns and height of 300 nm and with very low roughness. The samples were studied with

Wollaston probes by URCA. The impact of buried steps on thermal measurement was estimated by modelling. The results show the influence on heat flux dissipated by the probe into the sample is linked to the size of buried steps. The thermal profile from a thermal image was reconstituted also showing mastery of probe behaviour here as well as validity and relevance of the software implemented for SThM data analysis (refer to section 1-2). This provides a mean to characterize the sensitivity of a given SThM setup to subsurface features. The well-defined subsurface structures and the absence of sample topographic features also allow determination of probe thermal resolution, related effective thermal radius and probe-sample thermal contact resistance.

The High Thermal Contrast Sample, the Oxide Steps Sample and Buried Steps Sample are mature prototypes with TRL4 for the project. They constitute the KER N°3 “Passive reference nanostructured samples” of the project.

A ***Buried Bevel Sample*** (version of the buried steps sample) was also designed and fabricated. The fabrication was done by combining FIB, PECVD SiO_2 and subsequent CMP. The Si bevels were fabricated with dimensions 0.3x10 μm^2, 0.6x10 μm^2, 1.0x10 μm^2, 4.3x10 μm^2, 10x10 μm^2. The sample displayed small roughness (some nm), so, there is no influence of topography on thermal signal, with thermal contact resistance being the same everywhere. The experimental investigation showed a change in thermal signal according to the depth of buried features. The thermal profile was then reconstituted via modelling.

Furthermore, Pt thermoresistive probe measurements of epitaxially in-plane grown SiGe wires. When depositing Ge, horizontal wires grow from AuSi seeds that are obtained by annealing Au layers deposited on Si surfaces. SThM studies together with STEM images and EDS chemical analysis allowed relation of the SThM contrast with the morphology and composition of the nanostructures, both, laterally and in the vertical direction.

(ii)Investigation of roughness impact on measurement

As with topography, the roughness of a sample can have a strong effect on measurement with SThM. In order to obtain preliminary measurements of this effect, point measurements on substrates of SiO_2 and Ge with three levels of roughness were performed. Results clearly showed a reduction of heat transfer from the hot tip to the sample with increasing roughness, showing an increasing thermal resistance at the probe-sample contact. Thermal signal for SiO_2 of low thermal conductivity was however less impacted by this roughness effect. Three types of other samples were investigated. First type consisted of 2 different roughness levels obtained by grinding & polishing. Roughness and thermal conductance were measured, with some correlation being found - a slight trend of higher roughness areas having a lower thermal conductance, whilst lower areas showed, in general, a higher thermal conductance. Conclusions from two partners were identical proving the consistency of the used measurement method. However results had shown that these samples are not suitable for assessing the effect of roughness on SThM measurements due to the fact that they were produced by scratching the sample in one direction, rather than by random roughening. Samples with more random roughness were then produced from Si wafers using anodic oxidation and silicon dioxide removal. They were distributed to partners participating in the measurements led by the test plan for thermal SThM measurements. By analysis on different instruments and using different probes it was found that presence of roughness leads not only to increased variance of the apparent thermal conductivity, but also to its systematic shift. However, the shift dependence on roughness was highly influenced by the ratio between correlation length of the roughness and apex radius of the probe (confirmed also by numerical modelling for similar surface topography and probe geometries). These results can be used as an input for the uncertainty budget; in special cases of measurements on particular sample roughness and with particular probe types even a correction factor was found, however this did not have a general nature and was valid only for specific probe/sample combinations. The third sample type emulated roughness by Si cylinders with 50 nm height and diameters of 20 nm up to 1000 nm and spacings of 1:1, 1:2 and 1:3. Samples were fabricated on Si by e-beam lithography and dry-etching. Samples were characterised by the vacuum nulling system and probe (developed in WP8) and the combined SThM-SEM instrument (developed in WP8) and a KNT probe and with a Wollaston probe under air conditions. Results showed that the smallest features on the sample had little/no impact on the measured signal but 100 nm diameter features and larger had a very large impact. The analysis of data obtained from this sample is currently ongoing.

(iii) Analysis of 2D Structures

For testing SThM on well-controlled 2D structures, strain-tuned single crystalline Si nanomenbranes (7-100 nm thick and 100-500 um diameter) were fabricated (***attachment14***). To characterize the stress of the nanomembranes Raman scattering and ultrasonic force and force modulation microscopy characterizations were made. These measurements confirmed the good quality of the samples. For benchmarking with SThM, a thermal conductivity measurement method based on Raman microscopy was developed. Single and two laser Raman thermometry experiments and single and two probe SThM characterization were then performed. The effect of native oxide on the thermal conductivity of Si nanostructures was revealed by the two laser thermometry. Raman and SThM results were compared. Single SThM probe and single laser Raman results were difficult to benchmark with respect to each other due to apparent differencies of these methods. On the contrary, the two probe techniques compared well producing thermal conductivity of 37 ± 3 W/mK (34 ± 8 W/mK) for 47 nm-thick membrane.

(iv) Investigation of native oxide impact on SThM measurement

To test the effect of native oxide on SThM measurements a procedure involving H terminated Si surface was designed. Here Si wafer was dipped in hydrofluoric (HF) acid to remove the oxide and create the H-termination. At first ambient environment force spectroscopy-SThM was performed on HF treated and pristine native oxide regions. Only a slight difference in thermal response was noted due to native oxide, within the range of measurement error. Next, Si sample was directly put, after HF, under high-vacuum (10^{-5} Torr). Using two different heating levels, FS-SThM measurements performed on HF treated Si after different air exposure times that gradually allowed oxide formation on the Si surface. showed that native oxide growth on the Si surface is creating an extra boundary resistance that limits heat transfer between the probe and the sample. In order to fully understand this study, atomistic modelling is required. However, we demonstrate the impact of native oxide on SThM measurements.

(v) Analysis of composite thin films on substrate

The goal here was to test SThM to investigate the heat transfer within thin nanostructured thin films. Selected samples consisted of a mesoporous Cr layer (1, 2 and 5 nm thick) on PS-b-PEO block copolymer thin film (30 nm thick) on a Si substrate. The first samples fabricated and studied were thin PS layers on Si and glass substrates. X-ray reflectometry and SEM analysis showed that the obtained PS layers films exhibited continuous and flat surfaces with roughness ranging from 0.2 to 0.4 nm. SThM measurements under ambient air conditions were performed. The effective thermal conductivity of the samples as a function of polymeric film thickness was estimated showing that a variation of the effective thermal conductivity of 0.002 W. $m^{-1}.K^{-1}$ can be detected.

PS-b-PEO block copolymer thin film on a Si substrate with and without Cr deposit (***attachment15***) were fabricated. The microanalysis showed that BCPs microphase segregation on its constituent blocks originates periodic arrays of cylinders or lamellas with features size as small as sub-20 nm. It was observed that the Cr deposits preferentially on the PS matrix leaving the PEO cylinders uncovered. SThM characterization was carried out by Pd resistive and doped Si probes DS probes. The point measurements showed a similar trend of decreasing heat transfer as the metal layer thickness increased. This result is possibly related to a dominant effect of the Si substrate. SThM measurements in high vacuum environment with DS probes were also performed indicating an increased impact of the heat spreading into the metal and reduced Si substrate effect when Cr thickness increases. Considering the small tip apex of the thermal probe (~10 nm), it is reasonable to assume that the tip-sample thermal exchange is localized at the point of contact. Particularly, in high vacuum experimental conditions, the heat transfer through the liquid meniscus and air is eliminated and, negligible conductance occurs through radiation, so the dominant heat transfer mechanism is the conduction due to the mechanical contact of the probe with the sample. In this case, the heat source size is comparable to or smaller than the BCP+Cr top layer and the influence of the Cr layer dominates over the substrate. Therefore, the increase of the Cr layer thickness enhances heat spreading within the top layer at the expense of the heat spreading into the substrate. The measurements in high vacuum on bare and metal-coated BCP samples allow the thermal imaging of the two segregated phases of the BCPs with sub-20 nm thermal spatial resolution. The contrast in the thermal images seems to be related to the modulation of the BCP layer thickness.

(vi) Analysis of the effect of different levels of crystallinity of a polymeric material on the SThM measurements

The effect of different levels of crystallinity on the thermomechnical properties of a polyethylene material was also investigated based on the analysis of low-density polyethylene (PE) samples produced using 4 different cooling rates. Results of DSC, nanoindentation and SThM using DS probes showed that the melting point and mechanical properties of the PE specimens was unaffected by the different cooling rates used to mould them, although the degree of crystallinity of the specimens decreased significantly with increasing cooling rates. This indicates that the specimens are homogenous at the scales of the measurements performed. X-ray analysis determined the lamellar thickness of the crystalline regions to be lower than 50 nm confirming that the sample volume heated by the DS probe during thermomechanical analysis is larger than this dimension.

Conclusion: Many SThM investigations were performed for the analysis of the passive test samples fabricated in the project. These works also supported the refinement of SThM measurement protocols and were accompanied by the required improvement of SThM setups within consortium as well as the development of modelling tools for SThM analysis of nanocomposite samples. Topography-free samples, including 3D sub-surface sample of nanostructured features, 2D samples: thin films on substrate and suspended membranes, 1D samples: nano-plots were all analysed.

Results obtained were then used for the analysis of industrial nanocomposite materials. The tools produced enabled the creation of new know-how and the analysis and evaluation of various types of SThM probes and equipment in terms of spatial resolution and sensitivity. The SThM detection of sub-surface features was also clearly demonstrated. The project has also clearly demonstrated and provided first evaluation of the contribution of contact parameters (roughness, oxide, nanometric in thickness films) to SThM measurement.

1-1.B CHARACTERIZATION OF SThM MEASUREMENT USING ACTIVE SAMPLES

The measurement of temperature using SThM involves complex probe-sample thermal interaction. As part of the QUANTIHEAT project, samples to accurately probe these interactions were successfully designed, modeled, fabricated and measured. Ultimately, two of these devices have been identified as key exploitable results of the project.

Principle of SThM temperature measurement studied: Temperature measurement using SThM probes is typically carried out using the probe in passive mode. In the case of thermocouple based probes, this entails measuring the thermocouple voltage generated by the probe and in the case of thermal-resistor probes (e.g. KNT, Wollaston and Si probes) sensor electrical resistance is probed using the lowest possible current maintaining minimal Joule heating (typically <mK). Two approaches can then be taken to measure the temperature of a sample (1) probe response can be measured as a function of a sample with known, controllable temperature, producing a calibration plot of response vs. sample T that can be employed when measuring samples with unknown temperatures. This requires the calibration and unknown samples to be very similar in material and temperature (magnitude and extent). Alternatively (2), if using thermal-resistive probes, the probe temperature response can calibrated using a heat bath, permitting accurate measurements of probe T to be made on a sample with unknown temperature. Probe T can then be converted into sample T by use of an appropriate model. In both these instances, the challenge lies in quantifying probe-sample thermal coupling (related to environment, sample material, probe characteristics, temperature magnitude and extent). This information is essential to identify tolerable differences between calibration and measured samples (method 1) or to build an accurate model (method 2).

The active samples developed during QUANTIHEAT were designed to provide samples with well known material charateristics and geometry as well as controllable and/or measurable temperature as outlined below. These could then be employed in SThM measurements to quantify probe-sample thermal interactions, ultimately feeding into thermal measurements as described above.

Sample development and characterization: Active calibration and test samples were designed through modelling, fabricated and characterized in WP7 accordingly the technical requirements specified by partners in SP1. Samples and techniques passed then for WPs 8, 9, 10 and 11 for further investigations and prototyping activities. These active samples are separated in three groups:
Device A: Temperature reference device with defined temperature zones and extremely accurate temperature definition.
Device B: Temperature reference device with high sensitivity heat flux measurement. Two different device types utilizing semiconducting and metallic sensor elements were produced, but with the same ultimate goal.
Device C: Temperature reference device with large temperature and frequency range.

DEVICE A – TRL 5: Modelling using FEA (Comsol) was performed during the design phase of device A, to ensure a suitably uniform temperature distribution. In this device, the accurate measurement of sample temperature was achieved through the use of a thermometer operating either as a Johnson noise thermometer or an RTD, with temperature controlled through Joule heated resistors incorporated into the device. To achieve a desirable temperature range, the entire active region of the device was located on a Silicon Nitride membrane, minimizing heat conduction into the supporting substrate. The thermometer was located symmetrically around a defined spot that could then be used as the site of SThM contact. The device included eight, individually addressable heaters – 4 small, 4 large – that could be used together or independently to generate thermal profiles of different size and extent. The device had maximum symmetry to offer the most uniform temperature distribution possible (***attachment16***).

The thermal resistance of the membrane was measured as 7×10^5 K/W. The temperature distribution obtained using FEA was also validated against Johnson noise measurements obtained from the device itself. SThM measurements using the device allowed a lumped model relating heat transfer between the probe and sample (in air) allowed SThM probe characterization as well as simulated and measurement data to be compared. This characterisation demonstrated that device A characteristics were as proposed, making it well suited to SThM probe calibration when using KNT style probes. Its ability to generate a heated region with well-known temperature and extent clearly demonstrated the impact of sample-probe heat exchange through the environment. From a usability point of view, device A was PCB mounted – allowing easier integration of the device into a wider range of microscopes and its driver instrumentation permits safe, easy use of the device. Results obtained using this device demonstrated it is capable of generating valid, quantifiable data. The completed device A and associated instrumentation is a key exploitable result of the project.

DEVICE B– TRL 4 (***attachment17***): Two high sensitive platforms dedicated to evaluation of heat flux between tip and sample were developed

Device B1: Basic FEA (Comsol) simulations were carried out on device B to predict its thermal resistance and temperature distribution upon contact with SThM. The B1 device consisted of a 50 nm thick, 10 µm × 10 µm SiO2 membrane, connected to the bulk substrate via four narrow bridges. The 10 µm centre was required to assist contact when approaching SThM probes to the device, whilst the bridges maximized device thermal resistance. Heating/thermometry was achieved through a Pt/Au thermocouple and Pt thermometer-heater on the membranes. Samples were fabricated with various bridge widths and lengths (<5µm to ~10µm) to offer a range of device mechanical strength and thermal resistance. Driver instrumentation was developed alongside the device allowing voltage input for Pt resistor power control and voltage outputs for Pt resistance and thermocouple voltage. This was necessary due to the fragile electrical nature of the device. The best devices exhibited a minimum noise floor of 2.5 pW / root Hz when heated to 500 K. Measurements in vacuum demonstrated that the device was capable of characterizing the thermal conductance of a probe in contact.

Device B2: Device B2 was based on a thin silicon membrane and constitutes a new extremely sensitive nano-thermoelectric thermal detector. The silicon membrane was patterned into beams, which supported a membrane in the middle of the device. These silicon support beams worked simultaneously as electric conductors required in the operation of the device. The device had a silicon-based nano-thermocouple for temperature measurements, and a silicon based heater resistor for local heating of the membrane (also for thermometry). In the course of the project these new and extremely sensitive nano-thermoelectric thermal detectors were demonstrated to be able to measure small thermal signals. Several batches were fabricated and the non-idealities observed in the devices were tackled and other improvements were added to the device designs. When operated in vacuum the power resolution (per unit (1 Hz) measurement bandwidth) was limited by the Johnson-Nyquist noise of the nano-thermocouple beams (~10 pW/rtHz). The experimental data extracted from the characterization step followed the expected thermal roll-off and the linear power response further confirmed the proper operation of the device.

In addition to the fabrication process based on single-crystalline silicon, a simpler and more cost-efficient process based on polycrystalline silicon was developed during this project. First SThM measurements were performed with these devices. The developed technology does not only have prospects in scientific instrumentation but it can also enable industrial and consumer products in different fields ranging from chemical sensing to IR imaging.

DEVICE C-TRL7 (***attachment18***)_Device C was completed in two steps (two generations of devices were fabricated and analyzed during the project), resulting in the fabrication of devices C1, C2, C3 and production a new type of device, C4. This new device consisted of fine platinum heating lines patterned by e-beam, for thermal resolution measurements. Several samples were delivered to multiple partners over the course of the project. Also first proof of concept of foil devices was realized (C-Foil). These were produced using Inkjet printing of gold lines on thermal insulating polyimide sheets. Device types C1, C2, C3, C4 were characterized by near-infrared thermometry, SThM and thermoreflectance.

The first designs of device C included a pad of material of different nature (Pt) on the top-centre of the heating area, to study the influence of surface material on SThM probes thermal contact resistance. The second design had a RTD patterned locally, centered on top of the heating area. The RTD provided the actual surface contact temperature, which allowed monitoring of the thermal contact efficiency and heat flux into the SThM probe when in contact with the chip. The design included a four wire-probing configuration for the integrated RTD. The third design consisted of a suspended circular standalone platinum membrane (150 nm-thick / 10 µm-wide) defined in the heater layer.

Final device C’s offered a series of active calibration samples which could operate over a large temperature range, exhibiting lower power consumption and high sensitivity than has previously been reported. The initial objective was to increase the device sensitivity to calibrate any kind of T-microprobe. This objective was achieved. When calibrating thermal probes, the extracted calibration parameter was the thermal response, which represents a ratio between the different thermal resistances involved in contact. Device C is also a key exploitable result of the project. Device C2 RTD top were used for DoE and IlC related to temperature measurement using SThM.

Results of DOE: DOE experiments were carried out to evaluate measured probe temperature as a function of device C2 temperature. The impact of (topographic feedback) laser power, probe size, environmental gas pressure and contact force on the measurement was evaluated. The results displayed no significant influence of laser power or contact force on the measurement at one partner site, as evaluated using ANOVA. However, it was found that the probe size, contact force and gas pressure all influence temperature measurement, with size and pressure dominating at another partner site. The difference in the results can be explained by the fact that these partners employ very different SThM probe types and experimental systems.

Conclusions: The active devices designed, modelled, fabricated and measured as part of the QUANTIHEAT project provided a valuable resource to characterize the complex probe-sample thermal interaction that exists within ambient environment. In particular, the data obtained fed directly into models used to interpret and quantify SThM scan results. They were also key in identifying weaknesses in currently established SThM temperature measurement procedures. Because of these results, two devices (A and C) were identified as key exploitable results stemming from the project.

1-2 MODELLING AND NEW SOFTWARE FOR SThM

In SThM, the tip-surface thermal interaction involves multiple heat transport mechanisms that depend on various length scales. These are: solid-solid conduction, conduction by the surrounding gas, thermal radiation and conduction through the liquid nanofilm formed by capillary condensation on the probe and sample surfaces (***attachment19***). With respect to conventional thermal contacts, the SThM tip-sample solid-solid mechanical contact has multilevel complexity and roughness down to the atomic scale may be important. Dependence of all of these energy transfer channels on the length scale is not an easy task to investigate experimentally and predicting quantitatively all their relative contributions remains generally out of reach for a newcomer in the field, which has precluded the spread of SThM as a quantitative technique. In QUANTIHEAT, effort concentrated on the development of numerical tools that properly describe the probe-sample interaction and the application of these tools to problems related to real SThM measurements. This included new algorithms, benchmarking of different numerical methods to check their suitability for SThM and creation of tools for further impact, e.g. developing online interfaces for the developed codes.

1-2.A NANOSCALE TO MICROSCALE HEAT TRANSPORT SIMULATIONS

As no common tool embodying all the heat transfer modes is available, an inventory of the modelling tools available within the consortium led to a guide allowing the selection of tools depending on their applicability and range of possible use. It was found that each of the four tip-sample heat transfer modes could be simulated by only few partners and showed the difficulty in comparing results obtained with the different techniques, partly due to different computational constraints in terms of configurations being tractable. However, a benchmark was initiated when the comparison was possible and a reference configuration was designed to compare the strengths of the heat exchange channels. An example of reference model is given in ***attachment20***. The aim was to calculate heat transfer as a function of varying tip-sample separation, similarly to a force-distance curve that includes both non-contact and contact parts (negative separation).

Various methods were considered for the heat transfer between the tip surface and the sample surface through air, depending on the size of the SThM tip and samples. For large scales, standard Finite Volume (FVM) and Finite Differences (FDM) Methods were used. The impact of the ballistic regime was considered by introducing into FEM simulations either a ballistic thermal boundary resistance (TBR) or leaving an effective gap between the tip and the sample. This model was applied successfully for bulk samples, used as thermal reference samples (***attachment21***), and to suspended membranes. The heat transfer through air at the sub-mean free path scale was analysed by Monte Carlo (MC) simulations solving the Boltzmann Transport Equation (BTE) in a way known as Direct Simulation MC method (DSMC), providing the computationally-demanding key reference case. This method was extended to be operated on the high performance computing system to be able to compute more complex geometries. In parallel, various levels of less-demanding approximate methods were developed. These partly include the ballistic limitation to the transfer from MC particle tracking to heat flux lines estimates. All these methods could be included in the benchmark.

The contact between the tip and the sample was also considered by various methods, which model both heat transfer within part of the tip and part of the sample. At the large scale, a FEM model was used for probe-sample calculations, establishing a set of standard problems for benchmarking different modelling approaches. A methodology enabling modelling of phonon heat transfer between a tip of hemispherical or cylindrical shapes and a parallelepiped sample was developed based on the Diffuse Mismatch Model (DMM) capturing some tip-sample interface effects. The smallest scale was addressed by non-equilibrium classical molecular dynamics approach suitable for calculations of heat transfer in very high resolution SThM images (obtained e.g. by carbon nanotube probes). The approach is based on a custom-built software.

In parallel, analytical models based on conductance networks fed partly by experimental data were used. In particular, an analytical model comprising the finite size effect of the Pd resistive probe out and in contact with a sample was derived. A model including heat dissipation in the sample as well as analytical estimates of the contact thermal resistance via acoustic mismatch, showing a correlation between the applied force and the conductance which can be ascribed either to the ballistic conductance or to thermal boundary resistance, was developed. An interlink of mechanical and thermal models for 2D-material SThM measurements was also highlighted.

The computational tools developed within the project were applied by all the partners to various experimental data sets obtained within the other workpackages, depending on suitability of each particular numerical tool. On some samples (e.g. buried steps sample) different software tools were compared in order to test consistency of the calculations.

1-2.B RADIATIVE HEAT TRANSFER MODELLING

This heat transfer mode is important for vacuum SThM operation. New open numerical software SCUFF-EM based on the Boundary Element Method was first benchmarked against semi-analytical solutions (spheres of arbitrary sizes, sphere vs flat sample, etc.) and some errors were found, which are now corrected in later versions. In order to understand how resonant tip-sample heat transfer works, the far-field thermal emission of a sphere was analyzed. It was found that classical radiation cannot be applied to objects smaller than 150 microns. Then sphere-sample thermal radiation exchange for objects in silica was computed. Spectral data and flux-distance curves could be obtained for dielectrics. The exact location of the exchanged flux emission and absorption was highlighted, making it possible to couple with conduction (albeit this step was not performed). Flux-distance curves showed a behaviour close to $1/d^n$, with $n<1$. This was compared to analytical Proximity Approximation (PFA), which provides a qualitative solution. In parallel, local randomized source for FDTD featuring blackbody radiation options to address infrared heat transfer was developed. The model was implemented into an open source software package GSvit publicly available.

1-2.C MODELLING IN NON-IDEAL CONDITIONS: these non-ideal conditions mostly encompass the effect of liquids and the characterization of non-flat samples.

The impact of the water meniscus was treated by means of an analytical approach, where the input parameters were determined from experiments measuring adhesion forces as a function of temperature. A more-real shape of the meniscus could be considered, in order to accurately calculate the tip-to-sample heat transfer through this “thermal channel”. However, the probe and the sample are still considered “macroscopic” because nanometric roughness is usually unknown. The contact thermal resistances dominate the volume resistance.
SThM can also be operated in water or liquids, and is termed in this case iSThM (for immersion). FEM analyses were performed for the SThM probe fully immersed in liquid and for partial tip apex immersion, useful for the case of artificially-high humidity where a thick meniscus layer is present e.g. for biology-related experiments. The model was compared with experiments to take into account the heater geometry and the electrical parameters of the probe. Studies indicated that moderate thermal conductivity samples (polymers, oxides, nitrides) will benefit from the low-conductivity immersion (organic liquids) allowing a good compromise between the lateral resolution and sensitivity. Higher thermal conductivity samples (Si, metals, etc) are appropriate to study with the higher thermal conductivity (aqueous based) solutions.

The case of non-flat samples was treated by developing a FEM toolchain employing sample topography to perform a pixel-by-pixel simulation of the impact of probe-sample geometry changes on apparent SThM measurements (topography artifacts). The FEM data were fed with some effective parameters to cope with the computational demand and showed impressive ability to reproduce the experimental data once the code correlated the topography image with the thermal image (“virtual image”). This was tested on a high performance computing system and used for analysis of SThM data on rough samples, artificial steps and carbon nanotubes. The data on the rough samples and the steps were compared with experimental results.

1-2.D FAST ALGORITHMS AND INVERSE PROBLEM

The computational cost of the tip-sample heat transfer computation is very demanding and efforts were devoted to speeding up the computations. First, a comparison of different fast methods of topography artefact removal in conductivity contrast SThM mode was performed. Three different approaches were considered: neural network treatment based on local surface topography evaluation, local neighbourhood volume method, and full calculation of the heat transfer by FEM using a mesh created from real surface topography. The efficiency and practical usability of these approaches were compared. Graphic Processing Units (GPU) were implemented. The Monte Carlo code for simulating the phonon heat transfer between a hemispherical tip and a parallelepiped sample was parallelized with the Message Passing Interface (MPI). However, it was found that the computation time with a multi-processor approach remains important: it ranges from tens of hours to few days for realistic problems, which forbids the use of this code to every SThM user.

Consequently, the development of two efficient tools for tip-sample computations by experimentalists, to help them to reproduce their data numerically, was the second part of the work planned. The FEM online COMSOL environment is a key result (KERN°11 of the project, ***attachment22***) for making the work usable within the consortium and outside it, both during the project end and after. The developed infrastructure allows easy incorporation of models and their running in a browser, which speeds up significantly the learning curve for newcomers in the SThM field and allows for comparisons and benchmarks much easily. The FEM codes include effective parameters obtained by the various advanced methods mentioned previously. The second tool developed is a client-server interface to graphics card solver built as a simple way to allow regular SThM users to access the advanced computing capabilities that were developed within the project (KER N°13, ***attachment23***). In contrast to the FEM online tools, it is related to topography artefacts in SThM, so it is a complementary software for fast estimates e.g. in pixel-by-pixel calculations of virtual SThM images. This is compatible with new SThM-related options that now appear in the Gwyddion software framework well known to many AFM experimentalists, and should help spreading the quantitative analysis of SThM experimental images.

1-3 NEW PROBES, EQUIPMENTS AND MODES

The purpose of developing new probes, SThM equipment, and measurement modes was to improve the quality and understanding of SThM by both enhancing traditional methods and widening the scope of techniques and environments. This allowed a better understanding of the physical interactions that define SThM, provided a sound basis for the modelling and testing activities in other WPs, and pushed the scientific boundaries by introducing all new techniques.

A key part to any scanning thermal microscope is the SThM probe. Activities to develop novel probes were split into two distinct efforts: a) to improve the quality and reproducibility of the standard probes by engineering modifications to commercial style probes to study and improve limiting effects (like thermally induced cantilever bending, and variations in the tip apex) and b) to make new probes that offer exciting opportunities to make thermal measurements in a different way (like non-invasive nulling measurements and temperature sensing using thermocouples rather than resistance thermometers at the tip apex).

Stepping a up a system level, SThM measurement techniques are enabled by the scientific instruments that drive the SThM probes and, although the commercial systems are useful for a range of applications, there is always necessarily a restriction in flexibility with OEM products. Therefore, it was crucial that new instruments and measurement modes were delivered during the project to enable studies of new materials and test out the new SThM probes, modelling strategies and test samples. Systems were developed for different environments (vacuum and liquid SThM), dual mode microscopes (adding SEM, force spectroscopy, and shear AFM) and providing useful practical enhancements like large area SThM. Combined with the partners who operated commercial systems, and an entirely new commercial instrument developed by one OEM partner, a wide range of techniques were made available to the consortium to be included in the scientific studies. The final outputs (probes, equipment and modes) feature heavily in the exploitable outcomes of the project. KNT are planning for new SThM probes to come to market shortly. A whole new OEM product was enabled during the exploitation phase by building on the collaborative scientific work.

1-3.A DEVELOPMENT OF NOVEL PROBES (*attachment24*)

Ribbed probes: Two generations of designs were focused on offering improved production yield and probe robustness. Advanced lithographic alignment to increase reproducibility was studied. Process engineering activity resulted in a new pop-out design at the wafer scale. Ribbed cantilever probes were assessed for their function using high temperature ‘Device C’ samples and distributed to consortium for complementary test and evaluation. Ribbed probes were successfully tested. They are one the main exploitable results of the project: KER N°6.

Nulling SThM probes: The first generation (4 designs) of nulling SThM probes, incorporating a thermocouple, 4-terminal Pt resistor and separate cantilever heater were designed, modelled and fabricated. Initial tests aimed at comparing actual performance with that predicted by FEA models showed that the probes performed as expected. Design concepts for the new SThM probe-drive electronics were explored. Probe operation and concept driver electronics were evaluated using modular systems that were eventually combined into a single instrument.

Fabrication and process refinement for the complex nulling SThM probes continues as part of the exploitation activities.

Thermocouple probes: This work focused on the improvement of micro-wire probes with resistive and thermoelectric sensors, both employing a Quartz tuning fork (QTF) for topographic detection and control over tip-sample force. QTF-thermocouple probes were assessed on samples prepared in-house and on active 'Device C' samples. In addition, different passive samples were analyzed, providing data on both the probes and samples.

1-3.B DEVELOPMENT OF NOVEL SCANNING SYSTEMS

Large SThM system: We cooperated on large SThM system development together with Central European Institute of Technology (CEITEC). Using a CEITEC special device (NMM-1) the position sample was controlled in relation to probe with single nanometer uncertainty over the range of 25x25x5 mm. This was combined with conventional SThM probes and with different infrared temperature imaging cameras coupled with custom-built germanium optics. Successful development and demonstration of the combined SThM/IR large area scanning system were obtained in the project. KNT Ribbed probes were evaluated for their function in this system.

SThM-SEM combined system (***attachment25***)**:** A detailed CAD design was produced together with planned characteristics for the development of this combined system. The combined SEM/SThM system was delivered and evaluated. Subsequent work upgraded the system by way of mechanical and electronic improvements. The ribbed probes were evaluated using this system. Probe mechanical behavior was directly observed and rough samples were investigated. Observations were also made of the contact between a microprobe (not heated) and a sample with the help of an ESEM and an SEM under various conditions of sample temperature and gas pressure. This allowed the observation that the water meniscus at the probe/sample contact is modified when the sample surface is irradiated. This agrees with some results in the literature, which suggests that the Kelvin equation (generally used to describe meniscus) is not applicable when irradiating the probe/sample system with electrons.

SThM in liquid (iSThM: for immersion SThM), Force-spectroscopy SThM mode and modes combining ultrasonic force microscopy and shear-AFM with SThM were studied. During these studies an active made in house probe holder and stage, which are temperature controlled, was shown to eliminate one of the significant sources of measurement variability resulting in reliable, reproducible SThM data. This active probe holder and stage constitutes the KER N°8 of the project. High-vacuum SThM with simultaneous shear modulation was used to study the true nature of the SThM probe-sample contact and related conduction pathways. Results are in the analysis of probe-sample interaction in SThM (refer to section 1.4 of the report)

A SThM platform allowing the various types of KNT probes was developed to be employed in the CSI AFM (***attachment26***)**.** Work was completed by CSI involving the development and implementation of new probe holders, drive electronics and application support to arrive at a new SThM microscope product based on an existing AFM platform. CSI focuse on low cost, flexible instruments that are ideally placed to expand the scientific base of SThM in the field. This instrument was successfully evaluated using project passive samples. This platform is the KER N°7 of the project**.**

1.4 ANALYSIS OF PROBE-SAMPLE INTERACTION IN STHM

Both categories of reference and test passive samples were involved in the analysis of the probe-sample interaction that is not completely understood. The main results obtained are the following:

High-vacuum with simultaneous shear modulation were used to study the true nature of the SThM probe-sample contact and related conduction pathways. As there is no water meniscus and air conductance in high vacuum, the solid–solid probe-sample conductance pathway was exclusively probed. Comparing shear forces and thermal conductance dependence on contact area at varied normal force, it was conformed that solid-solid conductance ultimately occurs via ballistic thermal transport at individual nano-asperities contact. Moreover, for nanoscale thermal probes, this behaviour was generally the same in the ambient conditions, suggesting that solid-solid nanoscale contact is the dominating heat transport mechanism in both vacuum and ambient SThM, providing a powerful tool for interpretation of SThM measurements in the nanoscale junctions.

We established a new methodology for studying and specifying the rate of heat exchanged between a probe and a sample through the water meniscus from the analysis of the temperature –dependence of capillarity force using a probe apex description based on Kelvin's equation. Experiments and simulations were applied for samples with different thermal properties, surface roughness and wettability to Wollaston, KNT and doped silicon (DS) probes. Results have shown that the water contribution in the probe-sample interaction is not dominant whatever the probe and its temperature are (for the probes studied). Results showed that the contribution of water meniscus in the probe-sample interaction is lower than the one of air, depends strongly on the probe temperature and almost disappears at high probe temperatures.

2_THERMAL MODELLING FOR NANOMATERIALS

For nanoscale thermal transport modelling, different atomistic techniques can be used – they include for instance Molecular Dynamics, with the both Equilibrium (EMD) and the Non-Equilibrium (NEMD) approaches. They model heat flow at the atomic scale and allow determination of physical properties, like thermal conductivity, offering the possibility of considering different boundary or volume effects and imperfections. The properties are evaluated via the Green-Kubo approach in EMD or using heat sources/sinks in NEMD. Classical molecular dynamics is however still an approximate method using some sets of analytical potentials representing particle interactions, which cannot fully cover the quantum mechanical nature of the nanoscale world. A partial solution is to validate the potentials using a quantum mechanics approach, e.g. using Density Functional Theory.

MD is limited to the atomic scale or to homogeneous materials. An alternative is to employ models directly treating phonons -the energy carriers in solids-, using information on the lattice and solving the Boltzmann Transport Equation (BTE) for phonons. Scales below the one required for diffusive Fourier regimes are therefore tackled with the BTE by means of various methods, solved either with deterministic methods such as the Discrete Ordinate Method (DOM) or by means of stochastic methods such as Monte-Carlo ones. Approximate models such as the Ballistic-Diffusive Equations or the Phonon Radiative Transfer Equation can be used to limit the computational demand, especially in suitable geometries such as 2D or 2D axisymmetric configurations.

All these approaches describing heat conduction are still quite far from those classically used to model SThM at present. Until recently probe sizes were typically larger than the energy carrier’s Mean Free Path (MFP), so that continuum models (e.g. Finite Element Method) were mostly employed for data interpretation of ratio of different heat losses, estimation of topographic effect on sample or solution of inverse problems in sub-surface imaging.

In QUANTIHEAT a combination of nanoscale and microscale methods at MFP and wavelength limits were targeted with up-to-date simulation techniques in SP3. With tremendous increase in computational power of computers (both PC and high performance systems), these more-complex multiphysical models can be solved in reasonable time. Based on the techniques available to the consortium and comparison of their abilities for nanomaterial study works dealt with the development of new advanced tools and semi-analytical toolboxes for the simulation of heat transfer and thermomechanical properties in nanomaterials of interest for the project.

2.1 SOLID NANOMATERIALS: ADVANCED SIMULATION TOOLS

Atomistic modelling was performed from ab initio (GULP software for fitting potentials from Density Functional Calculations for purposes of classical MD calculations of complex materials) to MD. We established a toolchain for MD calculations of thermal conductivity using the Green-Kubo approach, including setting up crystalline or amorphous material atomistic models and performing calculations on them using open source solvers (e.g. LAMMPS). A custom-built classical MD software for handling models of disordered media and interfaces was developed. The software was validated by use of Density Functional Theory packages Fireball and Abinit, which also serve as sources of some empirical interatomic potentials. The tool was compared to publicly-available packages like LAMMPS; the benefit of the custom-built package for the project is its ease of integration into other tools disseminated by partners.

Simulation of phonon transport at room temperature in various geometries was performed in the frame of the Boltzmann Transport Equation for phonons. The Monte-Carlo statistical method was used. The materials were characterized by their polarization-dependent bulk dispersion curves as well as their polarization, temperature, and frequency dependent relaxation times. The diffuse mismatch model (DMM) was implemented to model phonon interactions at interfaces between adjacent materials. The method enables simulating thermal conductivity, thermal boundary conductance (TBC) and thermal conductance of nanomaterials of various shapes: films, nanowires, multilayered nanomaterials. Semiconductors and amorphous materials were implemented, such as silicon and silicon dioxide, and their combination was involved in experiments during the project, for instance in experiments performed. Deterministic methods built on the Ballistic-Diffusive Equations (BDE), based on earlier works, and on the Discrete Ordinates Method (DOM) were also implemented in Cartesian 1D and 2D coordinates. A 1D BTE solver was developed for frequency-dependent BTE and with partially-reflective interfaces that can be specular or diffuse. The 2D BTE was implemented with DOM in the EPRT (phonon ‘radiative transfer’) approximation as a function of medium temperature. Implementation of adiabatic boundaries in 2D was made. A comparison between the two methods was performed and showed that the exact solution is more reliable. An analysis of the conditions of reflections at boundaries was performed in 1D, with specular as well as diffuse boundary conditions that were both implemented in the simulations performed within the gray approximation. Early comparison with experiments showed that they are mostly 3D in reality. Similar works were designed for 2D cylindrical geometries. These new tools were used in the last period of the project in complex geometries related to the project experiments, such as for the 3ω method.

2.2 SOLID NANOMATERIALS: SEMI-ANALYTICAL TOOLBOXES AT HAND

Various codes and semi-analytical modelling were developed to establish a chain of sub-continuum tools that can be included into FEM codes and allow the establishment of multiscale design law for thermal management in nanomaterials. A frame of semi-analytical BTE-based theory involving Mean Free Path accumulation function and Fuchs-Sondheimer boundary scattering model was developed. With this model it was possible to obtain the accumulated thermal conductivity as a function of the phonon mean free path, and therefore the thermal conductivity in Si membranes with the help of FEM simulations reproducing the two-laser thermometry experiments (refer to part 1-1.A.3 “Analysis of 2D Structures” of the report). We also performed analytical work related to phonon transport. We did some analytical work in 1D to analyse the impact of the film thickness on the local temperature profile. It showed that a crude approximation can allow providing the slope of the linearized ballistic profile. In addition, we developed a FEM code where the ballistic flux reduction is included ad hoc in thermal boundary conductance. We analyzed the temperature and size dependencies of heat conduction by phonons in thin films, multilayers and for finite circular sources in 3D, in order to fit the data and propose analytical laws of thermal properties. Size and temperature dependence of thermal properties were modeled with polynomials and logarithm-based laws. Coefficients of polynomials and logarithmic functions were determined from the best fit of thermal properties models to the experimental data available in literature for thin films, data obtained numerically with FEM, and solutions of the BTE for phonons computed with the Monte Carlo approach in a simple framework. It was shown that the analytical laws can be included in FEM tools (COMSOL for instance in the project).

Thermal Boundary Resistances (TBR) in phonon-based materials were addressed by various approaches. A common semi-analytical tool involving the Acoustic Mismatch Model (AMM) and the Diffuse Mismatch Model (DMM) was developed. In addition, an acoustics-based FEM tool able to consider arbitrary-shaped surfaces in 2D was presented, which showed the reduction of the transmission coefficient at roughened interfaces on the basis of the shape and not on energy conservation. As such, this tool fills the gap between AMM and DMM. We implemented the DMM in its Monte Carlo code solving the BTE for a bilayer involving silicon dioxide. Temperature jumps could be observed at the interface. The thermal resistances computed from Monte Carlo simulations were validated against available molecular dynamics results from the literature and showed consistency. In the last period of the project we analysed the capability of computing the TBR involved in many samples of the project with SThM nanotips, which proved to be extremely sensitive to this parameter.

The case of materials involving electronic conduction was addressed by means of a 1D heat transport model at the contact between two dissimilar materials. This model is a macroscopic two-fluid model with electrons and phonons on both sides of the junction. Microscopic details are buried in the macroscopic transport coefficients. The study was extended to tunnel junctions, where the common geometry involving a sandwich electron carrier-phonon carrier-electron carrier is exhibited. Two-temperature analytical models were implemented and generalized to the geometry considered. The study was not performed at the spectral level, but at the energy level due to the already-large number of parameters involved. Comparison with data from the literature allowed to determination of some of the electron-phonon coupling constants, and experiments were performed to verify the analyses.

Finally, the case of anisotropic heat conduction in multilayers close to the surface was addressed. A full 3D model and a simplified radially symmetric FE model were developed to analyse some of the project nanomaterials. This allowed identification of boundary values for interfacial thermal conductance essential for quantitative determination of thermal conductivities of layered materials.

2.3 THERMOMECHANICAL PROPERTIES FROM NANO TO MACROSCALE

Heat conduction and thermomechanical behaviors within polymeric materials were tackled by means of FEM simulation to analyse due to their amorphous nature, but some coupling with semi-crystalline phase was also implemented.

We developed a toolchain for pixel-by-pixel calculation of thermomechanical properties using coupled mechanical and thermal models. A procedure for linking classical molecular dynamics calculations of thermal conductivity of polymer crystalline domains with larger FEM models to simulate effects of their size, position and orientation in an amorphous matrix was produced to model the thermal and mechanical behaviors of the whole samples. The

development was done based on experimental data obtained for polyethylene. A toolchain for treatment of glass transition in FEM modelling of the nano thermal analysis via SThM was developed. This is based on coupled mechanical and thermal problem solution in an open source software called SfePy. Temperature-dependent Young modulus is at the heart of the code and was initially implemented based on literature. This tool can now be transferred for other materials. In parallel simulations of the thermomechanical heating of polymer layers by SThM were made. It was found that it required an analysis of the behavior of the DS probe and was done in strong relation with WP6.
Another sub-task was related to strain in solid materials and its consequence on thermal conductivity measurements. FEM and analytical simulations of strain in Si nano-membranes investigated in WP3 were also performed, being important for the analysis of the samples and their design, in order to avoid corrugations detrimental to the experiments.

2.4 MULTISCALE COUPLED PROPERTIES: COUPLING FEM AND SUB-CONTINUUM TOOLS

The coupling between the BTE codes developed previously and the FEM environment COMSOL was performed. This was first done for 2D configuration with the DOM code of CNRS, in particular for spectrally-integrated phonon transport, and extended to the Monte Carlo code, which is more complicated due to the stochastic nature of the results. Multiscale thermal transport from nanometer to human-size compatible scale is now possible through this tool. This is important e.g. for the 3ω method and for air-based SThM experiments, where heat conduction in the sample takes place across length scales spanning 3 orders of magnitude (from 10 nm to 50 micrometers).
In parallel, we worked with the FEM code vendor to deliver the technical possibility for installing a COMSOL server at one location with a parametrized model, which would be accessed by any partner across the QUANTIHEAT consortium. Key FEM codes developed were updated onto the online platform (***attachment22***). This tool will be maintained for some time after the project and more codes are being updated remotely by the various partners. Remote computations by FEM codes, capable of reproducing the heat transfer within nanomaterials are available and are expected to have a strong impact on the spread of analysis methods for SThM and other techniques measuring nanoscale heat conduction effects. Such tools easily allow remote SThM data analysis by all consortium and external partners. This constitutes the KER N°11 of the project.

3_NANOMATERIAL DEVELOPED AND /OR CHARACTERIZED

If the outputs of QUANTIHEAT were to be useful as practical standards in the real world, it was essential that they were formulated in such a way as to promote their adoption by non-specialists. QUANTIHEAT therefore aimed to develop “real” nanoprocesses and nanomaterials for industrial applications to investigate the relevance of SThM in resolving critical aspects related to manufacturing processes and thermophysical characterization. Accordingly, the project had demonstrator applications. It focused on consortium industrial end-user nanomaterials. Industrial end-user nanomaterials from outside the consortium were also used to showcase the new technology developed during the project.

3.1 MATERIALS FROM CONSORTIUM INDUSTRIAL PARTNERS

Project applications included:

- Thermal (T-) NIL resists, where materials are further advanced by the admixture of specifically tailored fluorinated additives that impart improved surface and (thermo-) mechanical characteristics to the thin topcoat layer of the imprinted NIL resist patterns.
- Novel interconnect materials based on metallized micron sized polymer particles, in which the thermal and electrical properties of the nanostructured metallization layers must be optimized,
- ALD materials, in which the exquisite sensitivity of thermal imaging techniques to atomic scale interfaces will prove to be a valuable tool for process development.

The developed techniques also aimed at supporting the characterization of a novel generation of nanostructured thermal interface and thermoelectric materials.

Fields of technology applications addressed in the project, together with their associated issues and needs in terms of thermophysical knowledge were first identified in WP1. Industrial partners provided specifications and requirements in terms of thermophysical analysis at the nanoscale for each material. Based on this information, the metrology challenges addressed in the project were identified. Emphasis was given to the potential of SThM measurements to investigate thermal properties at the nanoscale and to improve knowledge tailored to industrial needs. First samples were prepared in WP4 and characterized in parallel in WP4 and WP9. The first results were used to refine the sample preparation required for SThM measurement and identify solutions to metrological roadblocks. During periods 2 and 3 of the project, industrial partners developed new processes to improve their materials or processes. To evaluate the improvement of their products and/or processes and better understand heat transfer within their materials they provided products at different stages of development into the consortium for characterization and/or benchmarking.

Most SThM measurements performed on these samples were qualitative. The challenges for consortium SThM users was to adapt their experimental set-ups and measurement approaches to the specific geometries of these samples, whilst also developing the required SThM calibration and measurement protocol and evaluating measurement uncertainty. The main results obtained on internal industrial materials are given here for each project application

3.1.A NIL RESISTS

Only analytical methods like SThM can provide the local thermophysical investigations needed for nanoscaled polymer structures in an appropriate fashion. In QUANTIHEAT thermal and thermomechanical measurements with AFM and SThM were performed on test samples of T-NIL resist in which polymers are in reduced dimensions with tailored molecular architecture. Samples, differing in terms of molecular weight among other parameters and obtained in different imprint conditions, were studied to have a direct feedback from imprinted structures and not just from the bulk material**.** Special attention was paid to tailored fluorinated additives (admixed to the resist formulation) that strongly facilitate the demoulding step in the NIL process.

-TOPIC 1: THERMAL NIL RESIST FORMULATIONS: We focused on the advancement of new fluorinated additives for use in thermal NIL resist formulations. Their performance was evaluated by thin film and imprint studies. In this task MRT prepared various thin NIL resist films and imprints (film thicknesses of 200, 100 and sub-100 nm) using reference stamps featuring different types of micro- and nanostructures for different thermal and photo-curable NIL resists. Imprint evaluation studies were conducted through AFM measurements, nanomechanical analyses using Force Modulation Microscopy (FMM) and Force Spectroscopy (FS) and SThM investigations. The performed SThM measurements provided valuable information – particularly in terms of the evaluation of the apparent glass transition temperatures (apparent T_gs) of the different films finally prepared with different NIL resist versions, namely mr-I 7000E (containing no additive), mr-I 7000R (containing a commercial fluorinated additive) and the mr-I 7000RX (containing a designed fluorinated additive, ***attachment27***). Commercial fluorinated additive was shown to have a larger impact on the thermomechanical properties of the material than the tailored fluorinated additive. The same observation was obtained for samples with Si substrate. Moreover, the performed work strongly expanded the current knowledge on structure-property-relationships of additives, so that new design rules regarding the composition and the architecture of fluorinated additives could be derived and established. Due to the general nature of those design rules this new know-how can be transferred and implemented into other NIL resists, i.e. into already commercialized NIL resists and also into future NIL resist developments.

-TOPIC 2: EVALUATION OF NIL RESISTS FOR AREA-SELECTIVE (AS)-ALD: NIL resist samples described above were coated with Al_2O_3, ZnO, TiO_2, ZrO_2, Pt, HfO_2, Ta_2O_5. Some of the samples were investigated using HR-SEM and a quite large number of samples were studied via AFM measurements, after an oxygen plasma treatment of the samples. The analysis of different evaluation studies clearly indicated that ALD and NIL are highly complementary techniques particularly due to the topographic profile / relief of imprinted NIL resist patterns, so that often no absolute area-selectivity performance is needed for specific applications; a high or partial area-selectivity performance is sometimes already sufficient. Specifically, UV-curable NIL resist mr-NIL210 was shown to feature the best area-selectivity (AS)-ALD performance for ZnO and the lowest performance for Al_2O_3 while the thermal NIL resists mr-I T85 and PBS (experimental resist) showed best AS-ALD performance for ZnO and Al_2O_3 (***attachment28***).

-TOPIC 3: NIL STAMP COATINGS VIA ALD PROCESS: Our AFM and SThM results clearly indicated that the preparation of thin Al_2O_3 layers via ALD processes onto imprinted mr-NIL210 patterns and the subsequent preparation of different anti-sticking layers (via conventional and/or new techniques) onto the Al_2O_3 layers render these systems potentially useful as thermally and mechanically robust NIL working stamps. The SThM measurements further contributed to valuable feedback by evaluating the thermal characteristics thus verifying the required thermal robustness of the ALD-coated NIL stamps. Due to the general nature of this technology such kind of systems could also be transferred to other application fields – particularly for permanent applications where (imprinted) patterns are exposed to harsh conditions such as heat and/or a corrosive environment.

3.1.B ALD LAYER DEVELOPMENT

ALD is a process which coats the whole surface conformally (3D), by atomic layer of selected material, thus providing a method to realize, for example, Bragg structures with dimensions of the order of phonon wavelength on curved surfaces. The conformality of the laminate films had been demonstrated but so far it had not been applied to thermal management. Various structures were developed for the investigations of thermal properties of solid-state nanostructured materials and nanocomposites as well as exploring and challenging the capabilities of SThM measurements. Conformal thermally/electrically insulating and conductive layers for nanoscale structures (layered and amorphous films) were studied. The amorphous composites included more than two elements producing compositional fluctuations impacting thermal properties. The effect of geometry, porosity and corrugation, was also investigated. Selective ALD growth was investigated as well, involving ALD layer patterning by growth inhibition layers on polymers. The main obtained results are as follows.

ALD LAYERS ON SI SUBSTRATE ALO-AZO-ALO nanolaminates involving Al_2O_3 thin layers provided by PICOSUN were studied with SThM using the Wollaston and KNT probes, and with photoreflectance for result comparison. A set of Si-SiO_2 samples were also investigated by nanomechanical and SThM techniques and compared to photoreflectance. While the photothermal technique provided quantitative results, it was concluded for SThM investigations of all these samples that thicker ALD coating or less-conducting layers would have been needed for proper quantitative analysis. It was noticed a large uncertainty on measurement of thermal conductivity made using the KNT probe operated in dc regime and under air conditions. The conclusions regarding the limitation of thermal conductivity measurement with SThM are discussed in part 1.1.A of this report.

ALD ON POROUS AND CORRUGATED MATERIALS Various porous-Si samples, were coated with Al_2O_3 to optimize the coating process of very high aspect ratio structures. The initial set of samples proved that the Al_2O_3 layer (nominal thickness 20 nm) is continuous in the structure, however, thinner at the bottom of the pores. Stacks of Al_2O_3-TiN-Al_2O_3 and Al_2O_3-Ir- Al_2O_3 were also successfully deposited reaching 1:200 AR, and the results were published at ALD 2015 and ALD 2016, respectively (***attachment29***). After ALD coating, the samples were characterized by SEM, AFM in tapping mode and SThM with the KNT and Wollaston probes. However, the samples were initially hard to investigate due to their roughness.

Corrugated samples consisting of high Aspect Ratio (AR) trenches within the subsurface of Si substrates were also coated with ALD Al_2O_3, Al_2O_3-Ru-Al_2O_3 and Al_2O_3-RuOx. SEM studies revealed conformal coating from 1:35 up to 1:300, i.e. down to the bottom of trenches. Al_2O_3 coated samples were studied by SThM. Initial results are promising but the analyses have to continue before any conclusion regarding heat transfer within such nanostructures can be made.

3.1.C CONDUCTIVE ADHESIVE: IMPROVEMENT OF DEPOSITION PROCESSES AND METAL COATING QUALITY

Silver-filled epoxy adhesives, known as Isotropic Conductive Adhesives (ICAs), have multiple applications within microelectronics, power electronics and the solar module industry. Design of an ICA requires optimization of a number of factors including thermal and electrical conductivities, rheological properties during application, total metal content (a critical cost issue as noble metals are used) and thermo-mechanical properties. The approach of CONPART for the improvement of the ICA material properties is to replace the solid metal flakes by metal-coated polymer spheres, micrometric in size (***attachment30***), resulting in an adhesive with one order of magnitude lower silver content whilst also improving the mechanical flexibility and hence the reliability. Optimizing the metal film on the polymer particles allows improving the cost-performance ratio and requires an efficient technique to characterize the transport properties of the deposited metal film, itself initially composed of nanoparticles randomly distributed on polymer surface. We focused on the improvement of deposition processes and metal coating quality during QUANTIHEAT. To maximize the conduction (electrical or thermal, as these are equivalent for the metal) versus deposited metal, the metal layers must be as homogenous as possible. Electrical measurements on such small objects are very difficult, and the dynamics is too fast. In addition, the results are always hampered with the contact resistances. Thermal metrology was anticipated to be very useful as an alternative to characterize the metal quality, not least because heat diffusion is on a timescale that can be readily resolved.

Samples supplied for analysis were dry polymer particles with silver coating and conductive adhesives based on these particles. Morphological characterization works included optical and SEM investigations, topography measurements with AFM and Focused Ion Beam (FIB) investigations of the interface between particle core and coating. Techniques for measuring the electrical contact resistance of single particles based on a nano-indenter setup were developed (electromechanical characterisation) (***attachment30.3-4***). Thermal analyses of single particle using conventional SThM techniques were found unsuitable for measurement on single particles. Experiments combining SThM and exploiting an active device C developed in WP7 (***attachment30.5***) were then performed using a thermocouple probe in 2-omega mode and attempted using fluorescent nanoparticles. This last approach with measurement under vacuum was found to be promising, comparing metallized and non-metallized particles. It allowed measuring the variation of the thermal conductance of the sample depending on the metal coating thickness. It also proposed another away for exploiting the active devices developed in the project, providing a new method of characterization of the contact between a sphere and a substrate, and hence a way for identifying and analysing the possible adhesive film between the two contact points.

The interactions between particles in the adhesive were also investigated. We investigated the interface between two metallized particles using FIB and measured the effective thermal conductivity of isotropic conductive adhesive based on novel particles using steady state method (test stand TIMA^{TM}6) and non-contact transient method (Laser Flash). This work also included successful SThM measurements on cross-sections of the cured adhesive (***attachment30.6***). Obtained results demonstrated the thermal performance of the novel conductive adhesive developed as a viable alternative to traditional ICA. The thermal conductivity measured of more than 2.8 W/m.K for an adhesive containing less than 4% volume of silver, is comparable with that of traditional adhesives that use five times more silver. This is in good agreement with the values of effective thermal conductivity estimated by the modelling developed during the project. An analytical model for spheres in contact in a rhombic configuration was also developed. This model showed good agreement with the contact area observed in the FIB analysis and the measured thermal conductivity.

All these measurements contributed to better understanding of the mechanical, electrical and thermo-electrical behaviours of the composite materials, how to improve the cost-performance and how to enhance reliability in the final adhesive applications. They provided critical feedback to the plating process and enabled the modification and improvement of the process based on quantitative criteria. Based on these results, a set of new metal systems were developed to improve contact resistance or stability in different environments. These includes Au (without Ni), based on observations of negative effects of the nickel coating and Pd coated Ag where stability in humid environments are critical.

3.1.D THERMOELECTRIC NANOMATERIALS: The studied thermoelectric Bi_2Te_3 laboratory materials were synthesized from nanopowders by a solution crystallization route. The synthesis procedure was adjusted in order to vary the size of the particles in order to try to obtain different crystalline domain sizes in final bulk nanostructured samples. XRD characterizations showed indeed an increase in crystalline size domain in the sample series. Measurements were performed by thermoreflectance and SThM. Quantitative values of thermal conductivity obtained by SThM technique using the Wollaston probe are in good agreement with those obtained using photoreflectance and from the scientific literature; validating then the calibration and measurement protocol established during the project. They also correspond with the values expected. Results also confirmed that it is difficult to reduce the thermal conductivity of the ThermoElectric Cooler material by reducing the size of its grains.

3.1.E THERMAL INTERFACE NANOMATERIALS: The thermal interface materials to be characterized within the project were composites based on Vertically Aligned Carbon NanoTubes (VACNT) and polymer thin layers. Although the effective thermal behavior of the interface is accessible through, for example, a commercial thermal impedance analyzer, future optimization of the system requires a better understanding of heat transfer within each of the building blocks. Sample preparation was a critical point because the SThM characterization is very dependant of the roughness and the preparation of the interface can modify the structure of this interface. For these reasons, three kinds of samples were investigated: TIM-a: VACNTs on a substrate of silicon, TIM-b: Au or SiN/polymer-VACNTs on a substrate of silicon, TIM-c: Cu/polymer-VACNTs/Si. Main focus was on the first sample. Cross-sections of samples obtained by BEXP were analyzed using SThM measurements in vacuum with a doped Si probe. Based on these measurements and the use of a three spreading thermal resistance model for the description of the sample, the anisotropy of heat transfer in the VACNTS layer was studied (***attachment31***). The obtained values of thermal conductivity are in the expected range and the approach demonstrated the material anisotropy. This also validated that the doped Si probe operated in vacuum can be used for high thermal conductivity measurements. A specific set-up to measure the cross-section temperature on the composites TIM-b and TIM-c was also implemented. The ability to test full interface under a temperature change with this set-up was demonstrated but further analysis is required to complete the material analysis.

3.2 INDUSTRIAL NANOMATERIALS FROM OUTSIDE THE CONSORTIUM

To showcase the new technology developed in QUANTIHEAT a list of samples from outside the consortium was drawn up and four types of samples coming from four different industrial domains were prioritized (to advance the processing technology in the state-of-the-art semiconductor devices), assigned appropriate calibration and measurement strategies and measured during the last months of the project in WP11.

3.2.A ACTIVE MATERIALS IN OPTO-ELECTRONIC DEVICES: Two Molecular beam epitaxy grown group IV GeSn alloys were investigated using the Wollaston probe. Samples consisted of 3 layers grown on a Si(100) substrate: Si – 100 nm Ge – 100 nm Ge - 50 nm Ge and Si – 100 nm Ge – 100 nm Ge - 150 nm Ge with 10% Sn. GeSn alloy stability depends on the film thickness and the Sn content. Furthermore, if the films are annealed after growth, part of the Sn content can migrate as the film is metastable as was the case for the second sample studied.

As this sample was annealed after growth (to 400°C), it is very likely that part of the Sn migrated to the surface. Thermal imaging results (*attachment 36*) obtained showed that SThM can directly observe and then distinguish both materials Ge and Sn at the sample surface, localizing surface protrusions with high concentration of Sn. Consequently, SThM could be a potential method for speeding up the optimization process of such alloys. Further analysis to gain a better knowledge of the features observed at the sample surface (subsurface) in terms of shape and thickness is however required for a complete demonstration of this SThM potentiality and the quantitative measurement of the sample thermal properties.

3.2.A COATINGS USED IN THE LARGE-SCALE SEMICONDUCTOR INDUSTRY DURING WAFER PROCESSING were measured with the KNT probe. Results were in terms of thermal conductance from the probe to the underlying Si wafer through the thin spin-on film. As expected, thinner films (10 nm spin-on glass) gave a relatively higher conductance value compared to thicker ones (65 nm spin-on carbon and 65 nm spin-on carbon + 10 nm spin-on glass). In this respect, SThM has been shown to be suitable for assessing the thermal resistance of a composite layer on a substrate.

Nanoscale thermal transport is essential in the fabrication process of semiconductor devices. The development of new processing technologies relies on the thermal properties of the materials used. In many cases, standard techniques such as optical methods or electrical 3w methods are not suitable for the needs of industry which uses ever thinner films (<100 nm) and requires a quick turnaround of measurements for the development of the technology. SThM spectroscopy mode answers these challenges by providing a quick measurement solution sensitive to minute changes of thermal conductance. For example, a preferred spin-on layer can be chosen for its high or low thermal conductance based on the measurements performed in this exercise. Therefore, the technique can answer issues faced in many areas of semiconductor industry research and development.

3.2.B GRAPHENE DEVICE: Graphene is a true two-dimensional material with unique properties. The proximity of the charge carriers on the surface means it can be easily approached by SThM probes and its two dimensionality means the heat diffusion through the bulk can also be neglected. All these make graphene a good candidate to demonstrate the novel SThM techniques developed in QUANTIHEAT. Hall bar devices with channel width varying from 300- 1000 nm width in the chip pattern as defined using e-beam lithography on epitaxial graphene grown on SiC substrate were investigated. The new ribbed probe was used to show that, as expected, graphene exhibits higher thermal conductivity than the Silicon carbide substrate and gold pads of the sample (*attachment33*). However, for quantification of graphene thermal conductivity, more measurements must be taken and a novel calibration method for the nanoprobe must be found. A calibration of the SThM method using the oxide step samples and its associated modelling is a promising solution.

3.2.C A STANDARD THERMAL SAMPLE (CARBON FIBRE IN EPOXY) used to test resolution and thermal contrast from leading instrument manufacturer (Anasys Instruments) was also analyzed. Using the protocol developed within the QUANTIHEAT project, we were able to use SThM measurement with a KNT probe to estimate a value of thermal conductivity for the epoxy part of the sample as this displays a thermal conductivity in the range where SThM is most sensitive. The sample provided good contrast but it was difficult for the data obtained to be used to quantitatively evaluate the carbon fibre (*attachment34*). This is in line with the conclusions regarding the limitation of thermal conductivity measurement with SThM discussed in part 1.1.A of this report. One can also notice that the free-topography samples we propose as standard SThM test sample to test resolution and thermal contrast offer the advantage compared to the standard sample from Anasys Instruments as, in contrast, they are well-known sample (geometry and properties in subsurface), fully characterized and without topography.

The results obtained on external industrial samples were provided back to the providers of these samples. Based on our results, it is expected that this exchange will be a continuation of further collaboration between the involved partners and industrials.

4_OTHER THERMAL METHODS DEVELOPED

4.1 DEVICES FOR THERMOMETRY USING THE 3-OMEGA METHOD

The 3-omega method is a well-known method for the determination of the thermal conductivity of materials. For the traditional method a thin metal line functioning as heater and sensor has to be deposited on top of the sample. This is often impractical or impossible for very rough samples, liquids or pastes. The objective in QUANTIHEAT was to develop a universal platform for thermal conductivity and diffusivity measurements. Different chips for thermal measurement using the bidirectional 3-omega method were designed, fabricated and tested. The proof of concept for the bidirectional measurements with chips was shown. The thermal conductivity and the order of magnitude of the thermal diffusivity of different reference materials (fluids, pastes or gels) can be determined (***attachment35***). The objective was achieved even if further improvement of the chip uniformity can be targeted. The chip is ready for commercial exploitation (TRL 5).

4.2 THERMOREFLECTANCE SETUP

A thermoreflectance set-up was also developed in the frame of WP7 based on SP1 specifications for sample characterization. The technology was validated and fully demonstrated in laboratory on active devices (gold line on Si substrate) and compared to infrared thermometry (TRL4).

Each of the two developed methods constitutes a key exploitable result of the project (KER N°9 and KER N°10 of the project). Their exploitation plan was prepared within WP12 as reported in the next part of this report.

A Potential impact

QUANTIHEAT's main outcome was the establishment and implementation of a new metrology technology based on scanning thermal probing to characterize the thermal properties of nanomaterials, polymers, composites and devices at nanoscale. The new technology included measurement techniques, reference and calibration samples, measurement procedures, and good practice guides and modeling and simulation tools, leading to the creation of standards in the field of research on nanoscale thermal properties. All this was achieved during the project (***attachment4***) and gives impact in six main ways.

IMPACT1: Advancement of standardisation in the nanotechnology field

Standardization of thermal nanomeasurement technology is essential to increase confidence in the data and to underpin the intercomparability of data thus generated. Standardisation and its adoption by users will demonstrate and enhance confidence in the use of SThM methods and data generated thereby increasing the project impact through enhanced uptake of the measurement technologies.

The project provided two categories of reference samples for the verification of the calibration and measurement procedures, and the evaluation of SThM techniques. For each category of samples and depending on the results obtained, mechanisms for dissemination and transfer of samples to users were explored, evaluated and implemented.

REFERENCE SAMPLES_ Regarding the bulk passive reference samples, as the thermal properties of samples were estimated with their uncertainty, their ultimate use is not exclusively reserved to calibration and characterization of SThM: calibration and characterization of various thermal characterization techniques can also be performed with these samples. Consequently, an application note regarding bulk passive reference samples has been made available on the project website. From a practical point of view and for their exploitation in the domain of SThM, the arrangement of reference materials on a single holder rather than individual samples for each reference material had to be studied. The oxide Steps Calibration Sample designed during the project is in line with these specifications. This sample together with the Topography Free SThM Calibration Sample and Buried Steps Passive Test Sample form part of the mature reference nanostructured samples developed during the project. For this sample second category dissemination through leading Scanning Probe Microscopy instrumentation manufacturers, thereby has been chosen as it provides confidence in their measurement technology. In the first phase each of the contacted SPM manufacturers received showcase application notes of the prototypes, with an offer of a demonstration at the client/host site. This dissemination by an independent organization (e.g. an NMI) would have been preferable but would require a time-consuming certification process for each sample before it could be implemented.

GOOD PRACTICE GUIDES_ Experimental investigations and interlaboratory comparisons performed provided a wealth of information on the accuracy and precision of the test methods and identified best practice in measurements. This knowledge was captured initially in protocols prepared to facilitate the standards writing process and then in good practice guides. These documents formed the basis for submission of New Work Item Proposals (NWIPs) for standardization through the International Standards Organization (ISO) or the European Committee for Standardization (CEN, French: *Comité Européen de Normalisation*). They will be made available on the QUANTIHEAT and CMI websites.

TERMINOLOGY AND DEFINITIONS_ It is intended that the Terminology and definitions for SThM measurements, including the instrumentation, test parameters and the thermal quantities measurable by SThM developed during the project will be submitted for normalization to CEN or, preferably, to ISO with adoption by CEN via the Vienna Agreement. The latter option provides opportunities for more effective European influence over the global market via the standardisation process, as well as proving a wider international feedback to the project. Standardisation activity on SPM methods has been undertaken in ISO TC201 Surface chemical analysis, but this has not focused on scanning thermal techniques. This could be added. For now good practice guides include a section on terms and definitions developed during the project.

NEW INDUSTRIAL STHM OPTION_ Industrial partner CSI has developed new probes holders and electronics for various probes designed by KNT. The first module able to drive the ribbed probes will be available for the market in 2018. This will favor the dissemination of SThM techniques developed during the project within AFM community.

IMPACT2: Improved performance of processes and final products

The project guided, enabled and advanced the development of new processes such as those used by the semiconductor manufacturing industry (atomic layer deposition (ALD), metallization), nanoimprint lithography (NIL) mask coating, as well as semiconductor and energy (TI and TE materials). It also enabled the characterization of new-generation nanomaterials in the same domains.

ALD PROCESSES_ Project results have proved benefits and capability for ALD in conformal metallic deposition in high-aspect ratios (HAR) and conformal metallic coating of powders. PICOSUN have improved know-how of processes on dimensionally confined material systems. They have seen growing interest on HAR, powder coating and area selective ALD. They have gained interest among customers and researchers in different fields and markets, mainly due to the results presented at international ALD conferences. They also developed ALD metal processes (e.g. Pt, Ir and Ru) on HAR-structures. The project has produced new know-how, particularly on powder coating with metals.

NIL PROCESSES_ Thermal and thermo-mechanical aspects typically have a great impact not only on the processing of (thermal) NIL resists but also on the performance in post-processing techniques like the pattern transfer via anisotropic plasma etching (in a substrate material) or subsequent modifications by e.g. ALD-based techniques. The measurements and analysis performed in the project resulted in a deeper and more comprehensive understanding of the different thermal characteristics of a NIL resist, which is in turn a key requirement for its proper design and potential application.
Generally, the newly developed additive technology of fluorinated additives admixed to NIL resist formulations greatly improves the imprint performance of the NIL resists leading thus to a drastically lower defectivity rate which is a key metric for most industrial high-volume fabrication processes. Future product developments will benefit from the generated know-how. Moreover, within the QUANTIHEAT project important design rules regarding the additive technology for NIL resists could be established, which greatly reduce MRT´s overall development time and efforts. Consequently specific customized versions of NIL resist formulations can be developed more rapidly and the needs of customers and their applicative-specific solutions can be addressed thus much faster.
New processes for NIL resist coatings should enable wider utilization of the method among participants and their clients, which is expected to be worth more than 1 M€/y. The project then enabled an increase of industrial competitiveness for MRT through strengthened capabilities in innovative products and services: these include custom tailored UV and T-NIL products, know-how about product formulation developed during the project and properties.

COMBINATION OF NIL WITH ALD_ This opens up completely new applications and addresses current challenges in the field of nanotechnology. Importantly, the obtained results suggest that for a couple of potential applications no absolute area-selectivity performance is required. In addition, the topographic profile of an imprinted structure can be highly advantageous in terms of the fabrication of very specific patterns that cannot be equally achieved by other patterning techniques.
Semiconductor processes where e.g. Al_2O_3 processes are used usually have the following steps: EtchStop – ALD – Pattern definition in Photoresist – Etching - Stripping. These can be replaced with the developed ALD inhibition steps: Inhibition Resist - ALD - Stripping, which will eliminate the need for an expensive EtchStop layer, and the use of highly toxic etching process (usually HF gas), with toxic residues being left on the substrate. The cost reduction to the semiconductor manufacturing industry in the EU can be calculated to be >3 M€/y, and the process simplification will enable faster time to market with reduced cost. In this context, QUANTIHEAT has produced established design rules regarding the additive technology for NIL resists, which greatly reduces MRT's overall development time and efforts. Additionally, specific customized versions of NIL resist formulations can be also developed more rapidly so that the needs of customers and their applicative-specific solutions can be addressed much faster.

PLATING TECHNOLOGIES AND CONDUCTIVE ADHESIVES_QUANTIHEAT has also contributed through characterizations by means of various methods (TIMA, Laser Flash and simulations) to better understand the thermal and electrical behavior of CONPART materials, and how to enhance their reliability in applications. Knowledge gained was particularly important in the development of CONPARTs central technology, especially concerning the silver and silver-palladium coated particles and isotropic conductive adhesive (ICA) technology. CONPART is in early stage of entering the market with their novel ICA particles.

NANOMATERIAL CHARACTERISATION_ Knowledge of the thermal performance of new nanomaterials is an essential prerequisite for their use in many industrial sectors. The project has provided technology and tools to perform the characterizations of thermal properties of new insulating nanomaterials such those used for thermoelectric devices (by THALES as an example), nano-porous materials and materials for semiconductor processing.
This feedback has demonstrated that SMEs as well as Companies can benefit from the QUANTIHEAT results. This takes many forms through applications and products: new SThM calibration systems, modifications of current microscopes accordingly, test systems and methods for the thermal characterization of nanomaterials, thus permitting new thermal managements of a great wealth of systems, novel improved nanomaterial developments and processing.

The project should then contribute to an increase of industrial competitiveness through strengthened capabilities in innovative products and services.

IMPACT3: The move from 'trial and error' based product development to digital product development and product life cycle environment will dramatically reduce design costs

The project developed traceable measurement methods and sought to establish them as potential standards. Calibrated and validated models were furthermore implemented in existing open-source (Gwydion) or commercial (COMSOL) modeling and analysis equipment software. They have provided an agreed basis of communication between designers, manufacturers and users of SThM and nanomaterials. This will enable rational design.

IMPACT4: Reducing the barriers to accessing and deploying nanotechnology in products

Modern technology is driven by the miniaturisation of devices and systems with associated increase in local power density. Modern materials developments rely on nanostructuring to realise engineered materials that simultaneously satisfy multiple requirements (electrical, environmental, thermal and mechanical). From an industrial point of view, thermal management and the associated techniques (SThM but also other techniques such as the 3w method for solid and liquid thin film analysis and thermoreflectance and Raman spectroscopy setup developed during the project) are of prime and critical importance. Based on specific scientific and industrial needs, it is particularly vital today to develop a nanoscale thermal measurement technique. The examples related to project results include:

- NANOSCALE THERMAL CONDUCTIVITY MEASUREMENT ON NANOSTRUCTURED THERMAL INTERFACE MATERIALS (TIM)_ The latest generation of materials under development comprises nanostructured metallic inclusions and carbon nanotubes embedded within a matrix. The physical characterization of such structures requires nanometre scale resolution and high accuracy. Complete thermal measurement at appropriate scales such that performed by ULANC on TIM materials from THALES will provide a check on the design process and allow **design optimization** to better address thermal management needs.
- THERMAL MEASUREMENTS ON ACTIVE ELECTRONIC MICRO AND NANO DEVICES_ The characterisation of nanoscale thermal conduction paths in device structure will be increasingly important for future devices. Nanoscale thermal mapping and calibrated models such those obtained in QUANTIHEAT will allow optimization of the material choice and facilitate the design of structures. By eliminating the need for conservative design this will result in improved lifetime and reliability of devices with reduced production costs and need for testing.

SCIENTIFIC IMPACT_ The project scientific impact has also to be underlined. As demonstrated by the dissemination activities described in the following part QUANTIHEAT has brought new knowledge on different fundamental questions related to the micro and nanoscale domains. Furthermore the increasing demands of European industry and research sectors for qualified human resources in the area of heat transfer management for nanotechnologies were addressed in the project by several means: the project contributed to the training of scientists and engineers in leading European industrial and research laboratories working on nanoscale heat transfer measurement, modeling and management. The organization of events by the consortium also enabled the improved basic know-how of scientists.

B_Main dissemination activities

The dissemination of knowledge was an important part of QUANTIHEAT, and partners used a wide variety of both industrial and academic channels. Dissemination activities ran over the duration of the project and involved a close interaction of all consortium members in order to communicate the technical achievements. Specifically, the QUANTIHEAT consortium had proposed to:

- Advertise the project and the subject of its research worldwide to research institutions and private companies operating in the sector of nanostructured materials and to device manufacturers.
- Generate high impact, good quality publications in well-respected international journals.
- Raise awareness of Network's research, achievements, capability for leading edge metrology.
- Communicate the Network's activities and achievements outside the scientific R&D community to make the benefits of the project visible to the private sector and society in general.

In order to achieve these objectives, the identified means of dissemination were as follows:

PROJECT DISSEMINATION TOOLS

- A secure **QUANTIHEAT Website** (www.QUANTIHEAT.eu) was set up and maintained by CNRS where all consortium members posted their contributions and documents (***attachmentB1***). The scientific content was provided and maintained with input from all partners. The website served as a hub for information exchange among the partners, to keep them informed of the project status, planning and all other important issues. It has contained

information about the project and its progress, and useful weblinks. It was operational in February 2014 and was continuously updated by the project's office throughout the project. The website was intensely used for internal communication purposes and exchange of documents, but it has also offered public access to specific areas.
The public access areas was branded with project logo, advertising public initiatives such as workshops and symposia, and conference attendance, publications, CVs and job opportunities, , the list of publications / proceedings / chapters of books, application notes generated by the project.
The website has been used to distribute the public output of the project. This **comprises the good practices guides on the recommended use of the SThM and** calibration protocols and the application notes describing project prototypes.

• A **dissemination mailing list** was established for those expressing an interest in the project and included institutions targeted in the dissemination plan. This dissemination list includes external users registered on the website, allowing QUANTIHEAT to interact both with interested parties from the scientific community and with institutions and private companies interested in end-use and exploitation of the project results. A list of the companies/research organizations interested in QUANTIHEAT technologies was developed. 144 organizations were identified as potentially interested in QUANTIHEAT technologies. They were kept informed regularly with Newsletters.

• **The logo of the project** (***attachmentB2***) was created by the coordinator CNRS. This 'branding' has been used across all promotional material providing a focal point for external recognition of the project messages.

• An **e-newsletter** (***attachmentB3***) describing the plans and activities of the consortium, as well as upcoming events was issued every years (publication in February 2015, November 2015, November 2016 and November 2017).
Significant effort will be deployed by CNRS to maintain the function of the website and mailing list after the end of the project. This will provide support to the community by providing an interactive communication tool. We anticipate that this will found a new collaborative community.

DISSEMINATION TOWARDS THE SCIENTIFIC COMMUNITY AND INDUSTRY

QUANTIHEAT partners were very active during the four years of the project (***attachmentB4***). 309 dissemination activities were held: 49% were oral presentations and 24% were posters presented in leading European and international conferences (key conferences: MRS, eMRS, Therminic, Eurotherm, specific QUANTIHEAT session at several conferences) and in international exhibitions (usually co-located with major conferences). 76 scientific articles, reviews, chapters of book and other publications (Thesis) have already been published. Results obtained were promoted in leading peer reviewed journals reporting on nanomaterials, metrology, surface analysis, on micromechanics and microengineering, on thermal physics, and solid state physics: Physical Review Letters, Nano Letters, Applied Physics Letters, Journal of Heat Transfer, Measurement Science and Technology, Journal of Sensor and Actuators, etc. The abstracts of published papers are available on the QUANTIHEAT website and full manuscripts are made free-access through manuscript servers such as ArXiv whenever possible.

The following events were organized by partners:

- **A scientific school** on "Thermal Instrumentation and Metrology for Micro/Nano: fundamentals and applications" organized **by the coordinator CNRS** in Fréjus, France from 30th November to 5th December 2014 (68 participants of which many were QUANTIHEAT partners).
- A SThM session at the **bi-annual SPM workshop** covering SPM users from Central European countries organized **by CMI** in Lednice, Czech Republic in March 2015 and March 2017.
- The international Workshop on Nanoscale measurements of physical properties **QMNTIA** (Quantitative Micro and Nano Thermal Imaging and Analysis) initially planned in July 2015 (*Milestone MS20*) postponed to September 2016 because clashes with similar events (e.g. "EMRS Fall2015"). The Consortium decided to organize one day workshop at the next Eurotherm conference that took place in Greece in September 2016. 3 sessions (SThM novel instrumentations / SThM measurement / Other advances for thermal nanometrology & imaging) were organized **by GU/CNRS**.
- A **session on the "SPM nano-mapping of materials properties"** at the Microscience Microscopy Congress 2017 in Manchester within SPM meeting focusing on QUANTIHEAT area organized **by ULANC** in July 2017**.**
- Presentations by NPL at ISO biannual committee meetings for transfer of openly available knowledge to NPL's Industrial Advisory Group, representing UK industry, RTOs and academia.
- A SThM measurements **workshop organized by CSI** in Paris on 16th-17th November 2017.
- A **one-day seminar on Heat transfer and thermal management in micro- and nano systems** organized **by CONPART** in Norway in June 2017.

- **Demonstration during the QUANTIHEAT final meeting**: on CSI SThM technologies and Nanotest 3-omega characterization system with Device C'.
- Presentation of new equipments /methods to SPM manufacturers by KNT in November 2017: each of contacted SPM manufacturers received showcase application notes of the prototypes. A demonstration of the products at the client/host site, at dates still to be defined with the client/host, has been proposed.

OTHER EVENTS INCLUDING SEVERAL QUANTIHEAT PARTNERS WERE ORGANIZED:

- **A 2-day workshop entitled "Scanning Thermal Microscopy and Heat Transfer at Micro- and Nano-scale Network Workshop"** organized by **GU, ULANC** in York, UK in December 2015 with a strong participation of CNRS.
- Specific QUANTIHEAT sessions at Therminic2016 in Budapest, Hungary and at Therminic2017 in Amsterdam, Netherlands with scientific presentations by partners and a demonstration by Nanotest of the 3-omega characterization system and thermoreflectance setups developed in project.

The scientific coordinator participated to conferences to represent the QUANTIHEAT project & the Consortium: for example, at NN15 (Nanosciences & Nanotechnologies conference) in Greece in July 2015 and Therminic2015 in Paris where a session was organized for QUANTIHEAT presentations.

QUANTIHEAT PARTNERS ALSO PARTICIPATED ALSO TO EVENTS ORGANIZED BY EUROPEAN COMMISSION AND IN SURVEYS:

- Participation of CNRS in "Characterization Tools" sub-cluster discussion from EC "Characterization cluster" around European research and innovation activities: in Brussels in Nov. 2014 and at EuroNanoForum2015 in Riga, Latvia.
- Contribution of CNRS and CMI to EC Brochure of Materials Modelling.
- Contribution of industrial partners to the 4th version of the Review of Materials Modelling.
- Participation of CNRS to EU survey on nanotechnology research, innovation and market development, and regulations.
- Participation of CNRS to EMCC Survey of development needs for characterization.

To summarize the dissemination plan described in the DoW was achieved. One can also notice that 70 additional dissemination activities have already been planned by partners (refer to ***attachmentsB5*** and ***B6***).

C_Exploitation of results

The overall goal for the exploitation of the project results has been to facilitate the use of the most innovative tools and methodologies from QUANTIHEAT by the widest possible community (industrial and scientific) to achieve impact.

PROJECT EXPLOITATION TOOLS

- Participants from academia and public research laboratories have planned to further disseminate project results as part of their research and teaching activities.
- A viable technology transfer was created. All possible means for exploiting the resulting knowledge were considered and will continue to be considered by the consortium after the project.
- The partners identified and maintained an extensive list of European companies who are or could be interested in exploiting the QUANTIHEAT technologies. All these contacts were kept informed on the project work progress by the E-Newsletters during the project.
- An exploitation plan was initially described in the QUANTIHEAT DoW for each industrial partner and more generally for research/ metrology institutes. This plan was clarified, detailed and updated during the project (and will be updated after the project). In this task, the QUANTIHEAT Consortium requested to the European Commission to receive from the service of ESIC2. An ESIC2 expert (P. Moran) initially attended for the first time the 12-Month Consortium meeting to have an overview of the project. A specific meeting with this expert took place at the next 18-Month Consortium meeting in May 2015, to focus on and discuss the exploitation of QUANTIHEAT results and the development of an exploitation plan. Prior to this meeting, the Consortium clearly identified and described the key exploitable results (KERs) of the project. The KERs were presented and discussed during the meeting at an ESS seminar in Glasgow on 29th May 2015. KERs and associated documents were updated regularly during the project. The *attachment3* lists the fifteen final KERs generated by the project.

QUANTIHEAT KERs may be classed in direct and indirect KERs (***attachmentB7***).

EXPLOITATION OF DIRECT KERS_Directs KERs correspond to new outcomes that were conceived and engineered during the project and were mature at the end of the project.

Regarding Standards and methods, **KER1** (LNE, CNRS, GU and CMI) are **good practice guides and draft of ISO Standards** giving procedures for the use and calibration of scanning thermal microscopy. The good practice guides will be published prior to the ISO standards enabling early adoption of expert advice for users. They will initially be used as standalone products for SThM users. They will be available free of cost on the websites of the QUANTIHEAT project and of CMI in 2018 and could be used afterward as the basis for the development of standards by ISO that could be also published through national standard bodies such as AFNOR, DIN and BSI.

Regarding hardware or physical products, **KER3** (GU, VTT, URCA, CNRS, CMI) is a **set of three passive reference nanostructured samples for measurement characterization at the nanoscale**. Currently there are no readily available samples where the adjacent areas of different materials, or samples with well-defined surface or subsurface structure of different materials and minimal or no topographical contrast. The three types of passive reference nanostructured samples we propose provide high quality new samples that meet these needs and enable the measurement of the sensitivity to changes of the subsurface thermal conductance of samples and the analysis of the spatial resolutions (lateral and in depth) of SThM microscopes. These samples may also have some attractive features for the characterization of other scanning probe microscopy (SPM) methods (AFM electrical modes as examples). Market Size corresponds approximately with 300-500 samples in total globally in the SThM field and additional 100-200 samples for other SPM methods ~ 100-200 k€. Opportunity to sell test samples to the OEMs for inclusion with SThM microscopes is indisputable.

KER5 (GU, VTT, EPFL) are **active on-chip devices for SThM tools**. These devices are suitable for SThM calibration and they can form a platform that is a part of SThM experiments. Such devices are not available on the market. There are 100-200 actively used SThM systems worldwide. The active samples will initially be of interest to a minority of these: max 50 - 100 devices/year market. Some users need electronics (and software), which could come with price of ~ 5 - 10 k€. The electronics could involve initial 10 - 50 boxes for current SThM users then an additional 1-2 per year. However, standard rack mount multi-purpose instrumentation electronics (GU) is suitable for some active devices. There is no competitor now, but companies could duplicate if they want to. Papers published prevent competing patent. Distributors would be companies such as Agar. Some of these may be sold via SThM manufacturers –Park AFM, Anasys Instruments and CSI. GU, EPFL and VTT expect impact through the dissemination of the results and growth of the SThM community because of the enhanced capability offered by these devices.

KER6 (GU/KNT) are **new SThM Probes** positioned as upgrades to existing probes and change a single product in a suite of products to suit the experimental needs. Experience tells us that working through established AFM hardware suppliers provides application support and sales and marketing channels. AFM suppliers have indicated that they can sell such product into their existing customer base (circa 50 active SThM systems and growing). Technological advances of this nature can create new demand out with the existing SThM customer base. Prime AFM manufacturers are NT-MDT, Anasys Instruments, Park AFM and CSI. Cost of Implementation before exploitation will be larger than 100k€ to provide enough probes to OEMs to test and samples to customers. Some investment from AFM suppliers will be required if probes are combined with other products like driving electronics. Time to market is estimated about 1 to 2 years after project completion. Probe selling price is in the range of 130-200€ per probe. Background IPR for microfabricated consumables is owned by GU. No patent protection exists. Key processes, recipes, designs may be kept as trade secrets. Exploitation through KNT (in direct industrial supply of consumables) or tech transfer to 3rd party have been planned. License agreement with AFM manufacturers is possible for electronic measurement systems owner: GU (refer to KER 5).

KER7 (CSI) is a **commercial System Hardware**. Industrial partner CSI has developed new probes holders and new electronics for the various probes designed by KNT. The first module able to drive the KNT-SThM-2an probes will be available for the market in 2018.

KER8: The development of an **active probe holder and stage**, which are temperature controlled, allows eliminating one of the significant sources of measurement variability resulting in reliable, reproducible SThM data. All SThM users (circa 50 active SThM systems and growing) and AFM suppliers & manufacturers should be interested. The product positioned as an add-on to existing platforms. Project partner CSI may incorporate this in their system to make a differentiator to increase the market share. Alternatively, the current SThM manufacturers may add this to their offering. The cost is small due to limited number of components required and moderate software implementation. That may increase if demonstration units are needed (~2-3k€ each) to be sent out to suppliers due to differing microscope probe holder designs. Time to market is expected 1-3 years after project completion (marketing routes & potential discussions with AFM manufacturers if product is to be sold). Quicker if we decide to provide designs and software instead of physical product. There is no patent protection existing. Key processes and designs may be kept as trade secrets. KNT/CSI may be expecting to be a partner on products aligned to their probes/AFM systems.

KER9 (Nanotest, VTT) and **KER10** (Nanotest) are respectively the **3ω test chip for thermal conductivity measurement of hard/viscous samples** and the **thermoreflectance setup** for surface temperature measurement of passive and active samples. Nothing in this area/application is currently on the European market. Three products are intended: Material measurement service (30-50 k€ p.a.), Measurement system for the measurements of thermal properties of e.g. liquids, polymers, mold compounds, biological samples (chemical industry, microtechnology, biotechnology) (50 k€ for 3ω measurement system; 50k€ - 200k€ for Thermoreflectance setup plus measurement equipment)) and single 3ω chips (10 k€ p.a.) for further use. Time to market is estimated 2-3 years after project ending. Several patents exist which use the three-omega technique for proximity measurements but nothing was found for thermal conductivity measurements. Therefore a new patent is intended. Design and technology has to be kept secret (VTT manufactured the 3ω test chip technology and optimized the related processes). Several patents exist for methods based on thermoreflectance thermography, but are not an obstacle for service delivery as the basic technique is not protected.

KER11 and **KER12** (ULANC: setup and maintain an online tool, configurations proposed; main contributions: ULANC, URCA and CNRS; minor contributions: CMI and ICN). KER11 is an **online software tool for simulation of scanning thermal microscopy tip-sample interaction**. This includes developed interactive tools for modelling the heat transfer between the scanning thermal microscopy tip and the sample, accounting for the probe geometry, interfacial thermal resistance as investigated within the frame of the project. KER12 is a **simulation tool for heat transfer within nanomaterials**; in particular, those characterized in the frame of the project are being developed. Both KERs link standard multiphysics software with sub-continuum data stored in libraries for ease of use without the need for “learning new tools”. The graphical presentation of the results will also help users being trained in the SThM technology and the dissemination of the approach to the wider community. Product/Service Market Size concern about 20-50 groups as well as undergraduate and graduate students working on SPM and materials characterization. The tools are also useful for companies using SThM and designing nanoscale-heating devices. Currently they are only for the educational and non-commercial use through the web application of COMSOL at ULANC. They are free for consortium members and free to disseminate and analyse its usefulness. Once this phase is complete, the choice of price for access will be possible.

KER13 (CMI) is a **new open source software for real time and post-processing of SThM data enabling the prediction and correction of topography artefacts on SThM data**. No comparable products are available right now. All SThM users should be interested: complicated results interpretation is one of causes of minor uptake of SThM in practice and the developed software can substantially simplify data processing. The product is compatible as a software add-on with all current instrumentation via use of already implemented data formats. Time to market is up to 6 months after project completion. Everything will be distributed under GNU GPL. CMI expects to spread the data processing tools to the wider community and gain additional user experiences, ideas for algorithms, common research, etc.

Application notes of most of the above direct KERs were produced. Those related to SThM were/will be presented to Industrial SPM manufacturers.

Exploitation of indirect KERs:

KER14: MRT Exploitation plan_ Introduced innovation compared to already existing products/services concerns 2 topics.

Topic 1: NIL-resist improvement by tailored and rationally designed fluorinated additives.

The new NIL resist formulations developed in the frame of the project can be applied for more demanding application fields that tolerate only a very low defectivity rate. The new fluorinated additive technology can be implemented in different types of NIL resists, i.e. in already commercialized NIL resists as well as in upcoming and ongoing NIL resist developments. Thus, the great majority of MRT’s NIL product line-up will directly benefit from this new additive technology. MRT are very confident and optimistic, that the new NIL resists equipped with the new fluorinated additives will strongly appeal to most of their current customers and will also attract new customers (NIL users). The new NIL resists formulations will be ready for commercialization approximately 1-3 years after finalizing the project. As the absolute amount of the new fluorinated additives in the NIL resist formulation is quite low, the final product price will be not significantly affected by the admixed additive.

Topic 2: Synergistic combinations of NIL- and ALD-related techniques.

There is already a great demand in industry to implement conventional and area-selective ALD in fabrication processes as this would directly simplify process operations and would thus directly lower fabrication costs. New

NIL resists specifically developed for a use in ALD-related applications are supposed to require the typical period for a NIL resist development of approx. 2-3 years.
To the best of our knowledge, there are no patented IPR that have an impact on these two topics. The developed know-how on the fluorinated additives in NIL resists and also the specific know-how regarding NIL resist formulations for ALD-related applications are solely owned by MRT. The related know-how and technology will directly and preferentially be employed for addressing the requirements of industrial and commercial end-users.

KER15: CONPART Exploitation plan_ The traditional conductive adhesives are based on solid silver particles, whereas the new adhesive is based on silver-coated polymer core particles. This gives a number of benefits. The new adhesive reduces the amount of silver by more than 90 % compared to existing conductive adhesives. This has a significant impact on reduced material cost and environmental impact, and improved thermo-mechanical properties of the adhesive. The amount of traditional silver particles used by the adhesive industry amounts to several billion USD / year. The market for conductive adhesives is increasing significantly, particularly for the Microelectronics-industry and PV. CONPART are in the early stages of entering the market with their novel ICA particles that will be sold to adhesive manufacturers.

KER16: THALES Exploitation plan_ No technique other than SThM allows the quantitative characterization of nanostructured materials at the nanoscale. Thales expectations are to increase in the maturity level of TIM and TE materials and could be a potential consumer of the SThM technology developed. For all of the developments, THALES will primarily exploit the technology as an end-user through the activities of the subsidiaries. A reliable tool for in-line routine thermal metrology will certainly help TRT to increase reliability and lifetime of its systems.

KER17: PICOUN Exploitation plan_ Existing physical and chemical fabrication methods are limited due to problems in obtaining thin, dimensionally confined functional material layers with full conformality, especially on High Aspect Ratio (HAR) surfaces. Due to the self-terminating nature of chemical reactions, ALD has demonstrated the ability to grow novel, high-performance device structures function of which depends on high-quality, dimensionally confined material layers on HAR surfaces. New HW solutions and process solutions were developed and a selection of them were already available during the project. There is a strong potential in several large industrial markets such as MEMS exhibiting strong CAGR in 2015-2020. The overall size of the ALD market expected to reach $1 billion in 2016 with ~30% CAGR predicted for 2015-2020. Picosun ALD products are positioned in an excellent position for further market penetration with good price/performance-ratio and several new and unique HW solutions introduced annually. The main focus concerns four market segments: IC, MEMS, Lighting, LED, Displays and 3D parts and the implementation before Exploitation is estimated about 200-250 k€.
Background IPR for ALD HW design is owned by Picosun and protected by multiple patents, local and international. Key processes, recipes, designs are kept as trade secrets. Novel design and process solutions are also owned by Picosun. Selected items will be protected with patents. The exploitation of project results will be through Picosun and commercial partners, both within and outside the consortium, resulting in direct sales and new industrial applications. Publishing scientific results are owned by Picosun and collaborating project partners (mainly VTT, ULANC and CNRS).

OTHER KEY RESULTS were achieved during the project and can be exploited in other projects.
- New equipments developed and described in application notes: new thermocouple probe (FEMTO-ST), new probe nulling/8-Channel (GU), vaccum SThM & SEM (CNRS)

- New equipments improved with published results: SThM spectroscopy mode, shear-force feedback operation, SThM in liquid environment (ULANC), combined SThM/IR radiometry system (CMI),

- New know-how: QUANTIHEAT has contributed to the training of young researchers and scientists in various field of nanotechnologies and nanosciences. SThM users have learnt a lot on measurement methodology from their collaboration with National Metrological Institutes (NMIs). NMIs and Industrial partners have learnt a lot on heat transfer at the nanoscales.

- New scientific questions: Many questions are still to be considered. The main one is surely “How to determinate, describe and model a contact at nanoscales?” whatever is the physical property to be determined. QUANTIHEAT-2 should focus on this challenging question.

- New applications of SThM: Our new knowledge of SThM advantages and limits allows us to plan further research collaboration on THALES TEC nanomaterials and on nanomaterials and devices where SThM is adapted. This concerns optoelectronics and thermoelectric nanomaterials, heterogeneous and highly anisotropic materials, self-assembled molecular monolayers with ultra-low thermal conductance for energy harvesting, in plane and through plane thermal and electrical transport measurements on ultrathin heterostructures with highly anisotropic nanomechanical properties, to name a few.

- **New applications of the other thermal techniques involved**: Measurement modeling was adapted to passive and active samples specific to the project but samples were designed for some of them to allow the simulation of real materials and devices. These modeling and techniques can be now applied to analyze samples, devices from industry such as microelectronics and optoelectronics.

- **Design laws for thermal management in nanotechnologies and nanomaterials**: We now have the key knowledge required for the optimization of SThM probe design tailored for specific research parameters.

- **QUANTIHEAT Consortium** is an operational European scientific team. It achieved most of the objectives but it is important to note here that despite the many achievements made during the past four years, it is clear that, because of limited resources, many questions remain unanswered and promising emerging techniques remained undeveloped. Therefore, scientifically but also economically it is important to pursue follow-on activities in future projects supported by the European Community. New scientific challenges have also still to be explored. Based upon a successful, motivational and enjoyable collaboration during the project lifetime, the QUANTIHEAT partners are ready to explore these challenges in new projects.

The implementation of the QUANTIHEAT exploitation plan has already started through new funded projects and potential future projects arising from QUANTIHEAT results or collaborations (***attachmentB8***, Confidential).