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JRP-Coordinator	
Name, title, organisation	François Piquemal, LNE
Tel:	+33 1 30 69 21 73
Email:	Francois.piquemal@lne.fr
JRP website address	http://projects.npl.co.uk/solcell/
Other JRP-Partners	
Short name, country	INTA, Spain METAS, Switzerland GUM, Poland VTT, Finland NPL, United Kingdom PTB, Germany TUBITAK, Turkey Keysight AT, Austria AZUR SPACE, Germany FhG, Germany

REG-Researcher 1	Christophe Licitra CEA, France	Start date: 01 July 2014 Duration: 36 months
REG-Researcher 2	Guilhem Almuneau CNRS, France	Start date: 01 July 2014 Duration: 36 months
REG-Researcher 3	Diego Alonso Alvarez IC, UK	Start date: 01 Feb 2015 Duration: 12 months

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TABLE OF CONTENTS

1 Executive Summary

This project has supported an emerging technology in the photovoltaic (PV) solar energy sector that has the potential to be sustainable without government subsidies. It has developed traceable metrological infrastructure dedicated to the rapid advances made on highly efficient multi-junction solar cells (MJSC) that are based on III-V materials (so called III-V because these semiconductor elements are in groups III and V of the periodic table of chemical elements). These metrological tools will support an increase in the efficiency of MJSCs, while improving manufacturing processes and materials, thereby enabling PV solar energy to compete with traditional energy sources.

The Problem

Today's energy policies are based on three requirements: the energy should be (i) secure, (ii) affordable and (iii) sustainable. The use of PV silicon solar cells has grown rapidly at a rate of 40% per year over the past decade. However, this rapid growth is unsustainable as it is mainly the result of government subsidies and a reduction in the cost of PV silicon-based solar cells. In addition, the silicon used in the PV solar cells is unable to provide the required energy conversion efficiency alone (i.e. the ability to convert solar energy to electrical energy); in order to compete with traditional energy sources (nuclear, coal etc) their conversion efficiency needs to reach at least 50% (a value that is considered as a tipping point for wider commercial acceptance by industrial experts).

Concentrated photovoltaics (CPV) is an emerging technology in the solar energy sector that requires far less area per kilo-watt-hour produced than traditional PV, and has the potential to be sustainable without government subsidies. CPV uses relatively cheap optical lenses to concentrate sunlight onto highly efficient MJSC, which are solar cells made of layers of different semiconductor materials. The use of multiple semiconducting materials in MJSC allows the absorbance of a broader range of wavelengths, improving their ability to convert sunlight to electrical energy when compared with existing PV silicon solar cells.

III-V materials based MJSC structures are complex, and prior to this project it was difficult to characterise their performance (and solar energy efficiency) with the required accuracy. In addition, there was a lack of reliable material properties data for the compound semiconductor materials used; i.e. discrepancies of around 30 % were observed between measured and modelled solar cell energy efficiencies.

Rating the performance of PV solar cells is critical for determining the cost per unit of energy, and an understanding of their solar energy efficiency is used to assess the relative performance of the different materials used. Prior to this project, only reference solar cells for MJSC calibration with a maximum of three active layers were calibrated in NMIs across Europe. However, these measurements showed lower calibration reproducibility and higher uncertainties when compared with PV silicon reference solar cells. Increasing the number of junctions in MJSC, using innovative nanostructures or coupling PV with other harvesting technology such as thermoelectric (converts heat to electricity) could also increase their energy conversion efficiency to 80 %. Therefore, metrological tools were needed to support these developments, as well as new standards with lower uncertainties in energy efficiency measurements.

The Solution

The project set out to solve this problem by developing techniques to enable traceable and accurate characterisation of III-V materials based MJSC, from the macro to nanoscale, with the following scientific and technical objectives:

- To develop methods to accurately measure electrical transport properties of III-V complex materials: band-gap, work function, dopant distribution, photocurrent, etc.;
- To characterise composition, thickness, structural and optical properties of III-V materials in order to highlight the effect of defects concentration, microstructure and interfaces on the recombination mechanisms of charge carriers;
- To measure carrier transport between interfaces in MJSC and to characterise tunnel-junction properties;
- To develop reliable tools to measure size dependent electronic structures of nanostructured semiconductor quantum dots;
- To measure thermoelectric properties of III-V material and thermal transport across interfaces;
- To develop traceable and reliable calibration methods, and standards for determining device efficiency, linearity, temperature dependence and spectral responsivity of MJSC devices.

Impact

This project has established the measurement infrastructure required by European industries and research laboratories to accelerate the development and adoption of next generation MJSC with the aim at increasing the solar cell efficiency to 50% or higher:

- Three European organisations AZUR SPACE, AIRBUS and ESA have already demonstrated their interest in the synthetic calibration method for MJSCs developed in the project;
- The high gain transimpedance amplifier developed in this project to characterise optical properties of III-V materials through the measurement of photo detector currents is now commercially available from the company Hasseb in Finland, and the expertise of the project partners has already helped one end user, the Finnish solar simulator manufacturer Endeas Oy, to solve issues in uniformity measurements;
- Project outputs have contributed to changes in a draft standard IEC 60904-8-1, Measurement of spectral responsivity of multi-junction photovoltaic devices. The standard was published in May 2017. In addition a report on electrical Scanning Probe Microscopy based measurements carried out in the project has been provided to the secretary of IEC TC-113 (Nanotechnology for electrotechnical products and systems) and is available to the ISO TC 229 Nanotechnologies committee.
- Two good practice guides (on calibration procedures for MJSC and on best methodologies and protocols for measuring properties of complex III-V structures) were also written and are available on a specific exchange platform dedicated to the project.

The project has contributed to a better understanding of key III-V semiconductor transport properties in complex heterostructures, with particular respect to nanostructured material. The close collaboration within the consortium will continue on the metrology for electrical scanning probe microscopy and calibration activities related to MJSCs. Moreover, the technical reports and data resulting from the project are available to industry and academia across Europe, and will feed into standards bodies for even wider dissemination.

2 Project context, rationale and objectives

Improving solar cell efficiency and lowering cost endeavours, along with clean energy initiatives are the primary factors for the impetus in solar energy production to date. Photovoltaics have grown at a phenomenal rate of over 40 % per year for the last decade, but much of this growth has been sustained by hefty government subsidies. To become a technology that truly changes the way the global community generates most of its electricity, PV will become too large to be helped substantially by funding from any government, and will need to be cost-effective for bulk power generation without subsidies. Due to the advances made in increasing III-V multi-junction cell efficiency and the corresponding reduction in collector area, concentrator photovoltaic (CPV) systems promise dramatically lower costs, without government subsidies, than today's photovoltaic technologies.

According to the European technology platform on PV and the European Photovoltaic Industry Association (EPIA) roadmap, the global annual new PV capacity market will reach 84 GW in 2017. It is anticipated that the PV market growth will accelerate, not only in Europe, which is likely to install more than 200 GW of new solar energy by 2020, but also in many other regions with a particularly high market potential in the Sunbelt countries. To reach this global PV production capacity, EPIA expects utility-scale plants of large energy capacity production (> 10 MW) to grow much faster than rooftop applications. The current state of art silicon solar cell is not likely to meet this need, as this technology requires extremely large aperture area (1 GW of generated electrical power needs about 10^7 m^2 of aperture area). High-concentration CPV technology is expected to be the alternative to supply a growing fraction of the world's PV energy requirements.

At high solar energy concentration ratios (i.e. between 200 suns to more than 1000 suns), the efficiency of the solar cell is more important than its cost so that a multi-junction solar cell (MJSC) with higher efficiency will be more cost-effective than the silicon concentrator cell.

MJSC use a combination of III-V semiconductor materials to more efficiently capture a larger range of photon energies. They contain several p-n junctions with band-gaps that span the solar spectrum; each junction being tuned to a different wavelength of light. State of the art industry standards are lattice-matched triple-junction solar cells. They are still relatively expensive and their use has been mostly limited to niche markets such as space applications where they provide an exceptional high power-to-weight ratio. At the time of shaping this project, the MJSCs had reached the highest efficiencies ever achieved in PV: above 41 % was reported by FhG in Europe and by Spectrolab in the US; and successive world efficiency records of 43.5 % and 44.4 % have been reported by Solar Junction (US) in 2012 and Sharp (Japan) in 2013 respectively.

Due to the relatively inexpensive concentrating optics used to focus the sunlight on a very small area (a few square millimetres) of semiconductor material, the MJSC enables highly efficient CPV modules for terrestrial applications to be manufactured commercially. The solar cell however accounts for only 10 % of the overall cost of solar energy generation systems. A key element for further energy cost reduction is a highly efficient MJSC with 50 % efficiency or higher.

Power utilities are looking for energy diversity to meet peak demand, which could be addressed by the CPV industry provided there is a drastic reduction in the CPV levelled cost of electricity (LCOE). This depends mainly on innovations at the material wafer level to achieve high cell and module performance. This is critical for reducing costs, but proving a new technology takes time and the only way the CPV industry can prove the technology works is to provide guarantees and warranties. Thus, reliable metrology tools and methods for III-V material characterisation and cell calibration measurement, and their incorporation into standards are critical for providing CPV technology with the trustworthiness needed to convince investors.

Industrial and academic roadmaps have identified four directions to improve the efficiency of III-V MJSC:

- Triple-junction solar cell efficiency can be further improved by design optimisation of each sub-cell. This depends on

  i. combination of optimised band-gap energies for the three individual junctions;

  ii. low structural defect densities in the layers achieved by using better lattice-matching, metamorphic structures or mechanical bonded stacks;

  iii. fine adjustment of the thickness of the layers to increase the current production (effect on the absorption coefficient, the diffusion length and the degree of transparency);

iv) an optimisation of the tunnel-junction interconnects in terms of offset band-gaps and low resistance.

- Another design improvement is to progress to devices with more junctions as the efficiency increases with the increasing number of junctions. However, as the sensitivity to spectral variations increases with the number of sub-cells, it is important to investigate the possible gain in energy production before a decision is made on the number of sub-cells and the material combination to use. A further advantage of using III-V materials will be to hybridise the solar cell with a thermoelectric structure to improve efficiency.
- The efficiency of III-V MJSC devices could also be improved by incorporating nanoscale semiconductor quantum dots (QD). QDs are size-dependent electronic structures and therefore their optoelectronic properties are tuneable, which offers the potential for high photovoltaic efficiency by tailoring the properties of existing materials and the self-assembly of nanostructures.
- The overall cost of the cell could be reduced by manufacturing the III-V junctions on silicon instead of germanium; silicon is a substrate that is cheaper and also available in larger wafers. However, growing such materials on Si substrates leads to heavily defective layers with dislocations due to the high lattice mismatch between silicon and III-V materials.

The high number of layers in III–V MJSC structures makes optimisation very expensive and protracted. Optimisation is currently performed mainly by predictive numerical modelling, which is extremely challenging for these sophisticated structures due to the complex electrical and optical interactions between the different layers and the high number of material parameters to be considered. Moreover, for most new materials used in these complex structures, there is a lack of material properties data, which limits the modelling capabilities so that discrepancies around 30 % are currently observed between measured and predictive efficiencies. Thus, accurate and spatially resolved metrology is needed to determine reliable and complete III-V material data sets (structural, optical, electrical, optoelectronic and thermionic properties), particularly for all materials used in sophisticated state of the art MJSC and emerging devices. Metrological tools need to be developed to understand the transport mechanisms, the influence of quantum confinement and interface effects in these structures in order to accelerate their market adoption. Industrial and academic actors (IQE, Abengoa, Isfoc, Naps, Isofoton, ITME...) have highlighted this as a key factor to allow CPV technology to reach its potential.

Rating the performance of PV modules is critical for determining the cost per watt, and the efficiency is a useful parameter to assess the relative performance of different PV concepts. Prior to this project, only MJSC with a maximum of three active layers could be calibrated in NMIs across Europe, and the devices are measured in solar simulators and traceable to reference cells which are calibrated during balloon flights directly to the sun spectrum at Air Mass zero (AM 0). Under such realistic and consequently non-controllable conditions, lower calibration reproducibility and higher uncertainties of 3 % are obtained. In comparison, primary silicon reference solar cells are investigated for instance by differential spectral responsivity (DSR) which has a much lower calibration uncertainty of 0.5 %. Hence with the next generation of MJSCs already in production, the need for corresponding new standards is becoming more and more urgent. Indeed, low uncertainty measurement of MJSC efficiency is fundamental for the PV industry because for large solar cell energy production, tiny errors in cell efficiency measurement will rapidly translate into a huge quantity of lost/gained electrical energy. Furthermore, progress of successive world records for the efficiency of emerging MJSC developed by different research groups is often within the measurement uncertainties. Adoption of enhanced metrological tools and methodologies will allow R&D laboratories to make an effective and accurate evaluation of the conversion efficiency achieved enabling them to identify real and promising innovation routes in which to invest.

The international PV community has developed testing and calibration documentary standards for cells and modules (IEC 61215, IEC 61646, IEC 904…) for well-known technologies (*i.e.* crystalline and amorphous silicon). IEC and ISO have identified the need to develop specific procedures and standards for multi-junction solar cells based CPV to support this large growing market. Furthermore, the integration of III-V technology with existing CMOS materials could also lead to a range of breakthrough systems in digital electronics and in optoelectronics. The International Technology Roadmap for Semiconductors 2012 highlighted the strong need for the metrology which is required to develop III-V materials integration in standard CMOS production lines.

The goal of this project was to develop traceable metrological infrastructure in support of the rapid advances made on multi-junction solar cells (MJSC) that are based on III-V materials. The project aimed to develop techniques and methodologies to enable traceable and accurate characterisation of structural, optical, electrical, optoelectronic and thermionic properties of III-V material based MJSC, from the macro to nanoscale, in order to enhance efficiency of present devices and enable the production of next generation solar cells.

The scientific and technical objectives were to:

1. Develop methods to accurately measure electrical transport properties of III-V complex heterostructures: band-gap, work function, dopant distribution, photocurrent, and carrier density, diffusion length, doping dependent minority carrier lifetime, absorption coefficients and series-resistances. Accurate measurements of these physical parameters are of particular importance to deeply understand the electrical transport phenomena in these heterostructures;

2. Characterise composition, thickness, structural and optical properties of III-V material in order to highlight the effect of defects concentration, microstructure and interfaces on the recombination mechanisms of charge carriers;

3. Measure carrier transport between interfaces in MJSC and to characterise narrow tunnel-junction properties;

4. Develop reliable tools and workflows to measure size dependent electronic structures of nanostructured semiconductor quantum dots;

5. Measure thermoelectric properties of III-V material and thermal transport across interfaces;

6. Develop traceable and reliable calibration methods, and standards for determining device efficiency, linearity, temperature dependence and spectral responsivity of MJSC devices.

3 Research results

3.1 Objective 1: Methods to accurately measure electrical transport properties of III-V complex heterostructures

The objective was to develop techniques and methodologies to accurately measure the electrical material properties of III-V systems relevant to triple-junction (3J) solar cells and associated tunnel-junctions and to structures that have more than 3 junctions. The determination of the electrical properties such as carrier density, mobility, conductivity and sheet resistance as well as dopant profile, work function and electrical defects near the interface requires the implementing of measurement methods at macroscale and at nanoscale. These data are required to provide direct measurement of one of the main performance limitations (photocurrent) in multi-junction solar cells.

3.1.1 Methods to measure electrical properties at macroscale

For reliable density and mobility determination, which currently involves Hall effect and Van der Pauw techniques, REG(CNRS) from the Laboratoire d'Analyse et d'Architecture des Systèmes in Toulouse (LAAS-CNRS) in collaboration with LNE designed and fabricated p doped GaAs and n doped GaAs calibration samples. Measurements have shown a good agreement with the expected nominal doping levels.

For sheet resistance measurements GUM has adapted contactless microwave measurement methods, using single post dielectric resonators operating at frequency about 5 GHz. Measurements have been successfully carried out on multilayered III – V structures composed alternatively of undoped (insulating) InGaP and n++ doped InGaP layers and deposited on semi-insulating GaAs substrate. These structures were manufactured by EPI-Lab and the Institute of Material Science and Technology in Warsaw. The relative uncertainty of these measurements was found at a level of 3 %.

3.1.2 Methods to measure electrical properties at nanoscale

Only a few techniques offer the possibility to measure the electronic properties of a device in cross section with a lateral resolution of a few nanometres; an essential set of techniques are based on scanning probe microscopy (SPM), whereby a nanometre physical probe is scanned on the cross section of the device of interest. The project has focused here on three of these techniques dedicated for electrical measurements, *i.e.* electrical SPM (eSPM) techniques which comprised scanning spreading resistance microscopy (SSRM), scanning Kelvin probe microscopy (SKPM), and scanning microwave microscopy (SMM). Briefly SSRM measures the current between a conductive tip in contact with the sample under a known bias. SKPM measures the local work function that is the distance between the local vacuum level and the local electrochemical potential (Fermi level). These measurements can be used to reconstruct the potential profiles across contacts and junctions; however extreme care is required in the interpretation of data due to the potential convolution of the inner work function with surface potential due to surface reconstruction, trapped charges or artefacts introduced by the SKPM control loop. The SMM measures local impedances in the GHz frequency range. It operates with a vector network analyser (VNA) which transmits a RF signal to the probe and detects the reflected signal. The VNA determines the ratio of the incident and reflected signal, *i.e.* the scattering parameter S_{11}.

The current challenges are the low lateral resolution and lack of established traceability. Furthermore, these measurement methods have been limited to silicon to date and suffer from a lack of accuracy and traceability for other materials and especially III-V components. For example, quantitative measurements of carrier density of semiconductors are difficult due to the lack of calibration techniques and the only possibility is calibrations using regions of known carrier concentrations (test structures) in close vicinity (less than 100 µm distant) to the region of interest that will be measured.

Characterisations of material properties layer by layer have been completed on single-junction and dual-junction structures lattice-matched to gallium arsenide (GaAs) and relevant sample preparation standard operating procedures have been developed and successfully reproduced.

The samples investigated here were provided by FhG. They have three different layer structures as shown in figure 1, the first two composed of single junction (called SOL and GIPSOL) and the third one being a dual junction structure (TAN) *i.e.* a TANDEM structure, which is a dual junction composed of individual junctions (SOL and GIPSOL).

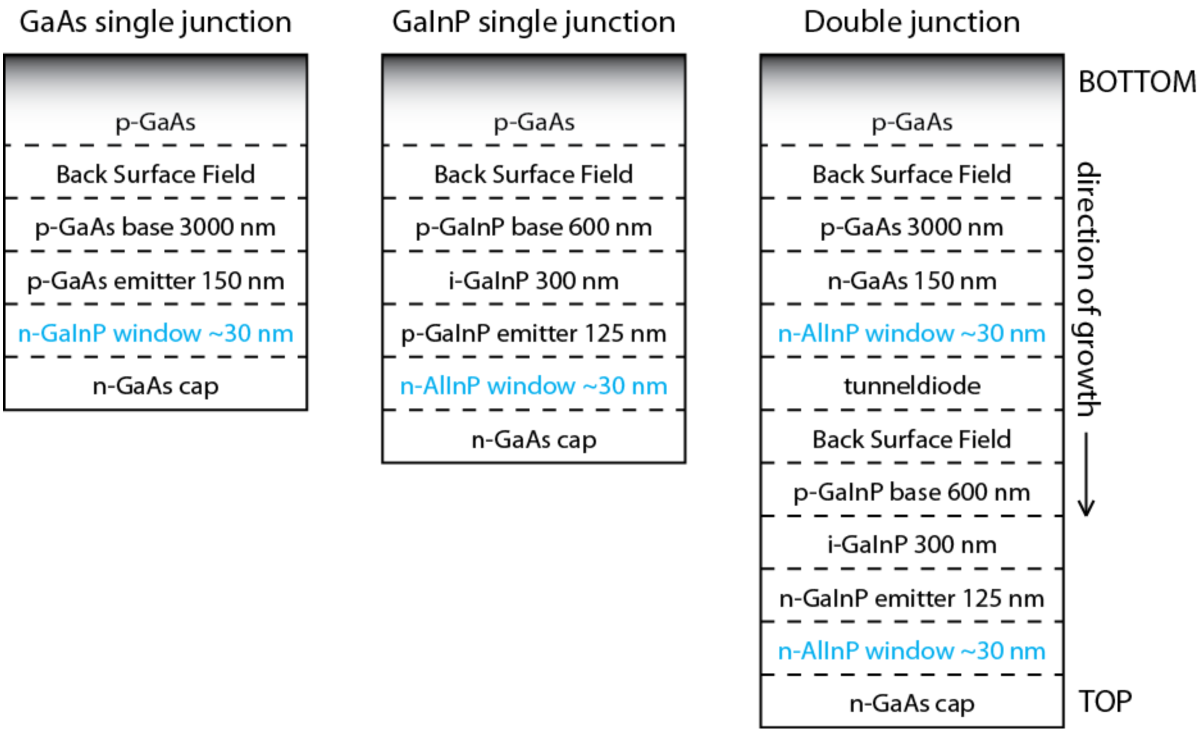


Fig. 1: Layer structure of the measured solar cells provided by FhG, left SOL, middle GIPSOL, right TAN.

New facilities were developed within the project for the nanoscale electrical characterisation of III-V samples. Successful implemented methods are SKPM in air and in ultra-high vacuum, SSRM and SMM. Uncertainty budgets and proper quantification of results have been established. All these methods aim to measure the dopant density at the nanoscale.

In order to calibrate these measurements, a GaAs staircase dopant density sample has been developed by LAAS. This reference structure has been successfully measured by Keysight Austria, LNE and METAS with SMM techniques.

A clear contrast between the different layers was visible (see figure 2) and plateaus in the data correspond well with the expected dopant densities and have been very well confirmed by secondary ion mass spectrometry (SIMS) measurements performed by REG(CEA) at CEA in Grenoble. An algorithm based on three known standards has been developed by METAS, which allows the extraction of dopant densities of semiconductor layers. For proper references, the accuracy can be below 10 %.

Using SMM techniques, it has also been demonstrated that a 50 nm lateral resolution could be achieved by scanning across a tunnel diode (width <50 nm) in TAN sample.

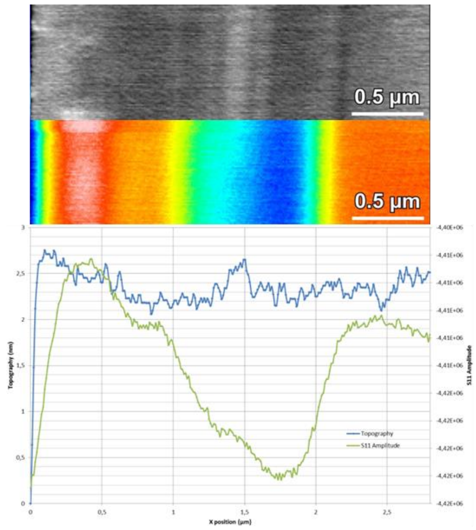


Fig. 2 LAAS p-doped GaAs staircase topography and S_{11} (amplitude) images and corresponding profiles.

The algorithm developed to extract dopant densities is an innovation going beyond state of the art. Furthermore no SMM results dealing with dopant densities in GaAs-based semiconductors have been published to date. A joint publication presenting the algorithm and the measurements on the GaAs staircase dopant density sample is in preparation.

At NPL, the first reproducible result has been obtained from SSRM based measurements on III-V materials (SOL sample) and has shown a lateral resolution better than 5 nm (figure 3). Due to the use of a logarithmic amplifier the technique is not sensitive enough to measure the difference in doping level between the layers. This was expected to be done by using SKPM techniques.

For SKPM, the preparation of the samples to obtain the correct data is critical and a method has been jointly developed by NPL, Imperial college and CEA for operation in air and in ultra-high vacuum. Prior carrying out workfunction profiles measurements on single and dual junctions, the method has been validated in terms of reproducibility and lateral resolution by using a reference multi-layered InGaAs/AlGaAs/GaAs sample manufactured by BAM. A maximal sensitivity of about 3 meV has been reached and the measured work function difference between GaAs and AlGaAs layers was found in excellent agreement with value reported in literature.

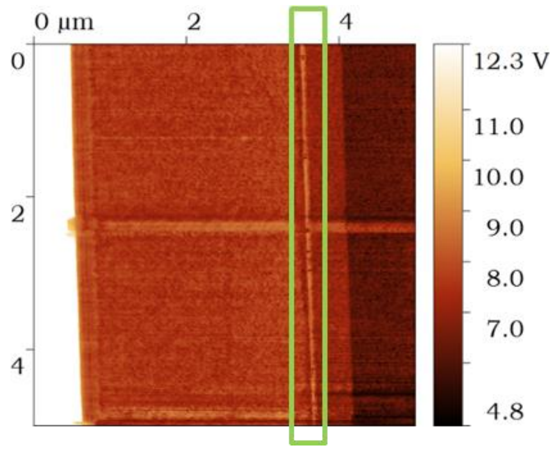


Fig. 3 SSRM measurement on SOL sample. A resolution of 5 nm was achieved on the Backscattering layer (BSF) of all samples green box. This was due to the very high doping level of this layer.

SKPM measurements have been carried out on TAN samples. NPL was able to measure contact potential variation down to 20 nm, with 20 meV sensitivity. In collaboration with REG(IC) at Imperial College, the experimental results agreed well with a band model of the system, allowing prediction of transport properties into the cell. The comparison of the theoretical and measured workfunction profiles has allowed one to estimate the doping profile in the different layers (figure 4).

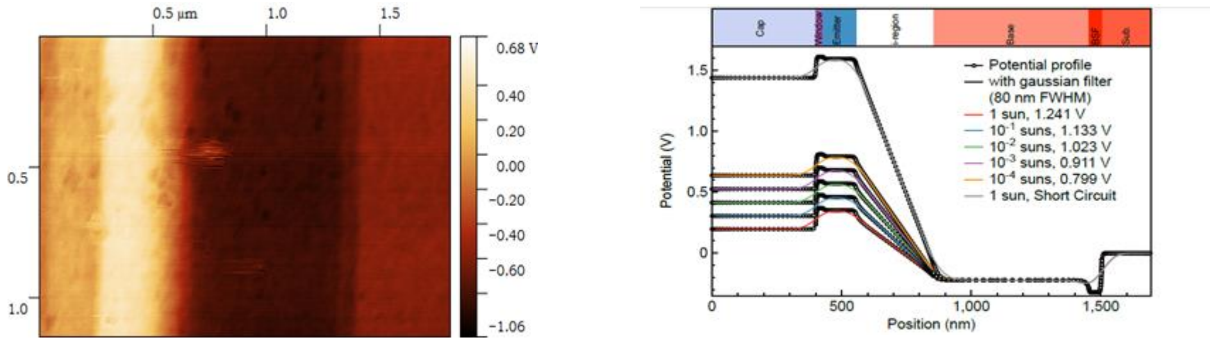


Fig. 4 Experimental profile TAN sample and theoretical profiles simulated. The theoretical profiles also estimated the variation under illumination – results not presented here.

Objective 1 Summary

The objective of developing techniques and methodologies to accurately measure electrical transport properties of III-V complex heterostructures has been achieved. The key results are:

- *New facilities at NMIs dedicated to the nanoscale electrical characterisation of III-V samples*. Three methods were successfully implemented using SKPM in air and in ultra-high vacuum, SSRM and SMM. Uncertainty budgets and proper quantification of results have been established.
- *New reference nanomaterials developed for the users of SMM in NMIs/DIs and in R&D laboratories from academia or industry involved in semiconductor sector*. For the first time, a GaAs staircase dopant density sample has been developed in order to calibrate SMM measurements. This reference structure has been successfully measured with SMM techniques.
- *First demonstration of suitability of SMM as metrological tool applied to semiconducting GaAs structures.* On the reference structure developed, a clear contrast between the different layers was visible using SMM and plateaus in the data correspond well with the expected dopant densities and have been very well confirmed by SIMS measurements. An algorithm based on three known standards has been developed, which allows the extraction of dopant densities of semiconductor layers. For proper references, the accuracy can be below 10 %.
- *Reproducibility and high sensitivity achieved from SSRM and SKPM measurements on III-V materials*. The first reproducible result has been obtained from SSRM based measurements on SOL sample and has shown a lateral resolution better than 5nm. From SKPM measurements performed on TAN samples. It has been possible to measure contact potential variation down to 20 nm, with 20 meV sensitivity.

3.2 Objective 2: Characterising composition, thickness, structural and optical properties of III-V material

Two categories of III-V material were considered by this objective: i) III-V systems relevant to 3J solar cells and associated tunnel-junctions and anti-reflection coatings, and ii) dilute nitride solar cells. To relate optical measurements to structural information, structural characterisation techniques are required and currently involve a combination of appropriate calibrated instrumentation.

3.2.1 III-V systems relevant to 3J solar cells and associated tunnel-junctions and anti-reflection coatings

Composition of III-V material

Composition characterisations of FhG samples using low energy SIMS, with enhanced depth resolution and determined layer composition and using photoluminescence (PL) and cathodoluminescence (CL) techniques for minority-carrier lifetime determination were performed by CEA.

SIMS measurements were carried out at CEA to quantify the dopant composition of the TAN sample provided by FhG and to characterise their quality of interfaces. The sample composition and the dopant concentrations were determined. The study reveals a complex structure of the back surface field (BSF) layer between the InGaP junction and the GaAs junction and the given stoichiometries in this area must be taken with care. These pieces of information were useful for the partners of the project, and particularly for FhG.

This task was not possible to be fulfilled without calibration samples. CEA supervised the fabrication of these necessary calibration samples thanks to a fruitful collaboration with LAAS and III-V lab in Palaiseau. Some of the calibration samples were synthesised by using ion implantations on epitaxies realised by LAAS. Other calibration samples came from the synthesis of in-situ doped epitaxies by III-V lab further analysed by the company Probion. Finally 12 different III-V calibration samples were realised and added to the SIMS library of CEA. This will help future quantifications of dopant concentration in III-V materials. Extensive SIMS analyses were performed on each of these samples. These calibration samples have also been used for collaboration between CEA and PTB to make a comparison between SIMS and Grazing incidence X-Ray Fluorescence (GIXRF). The complementarity of these two techniques to get accurate dopant profiles in implanted samples has been demonstrated.

CEA also applied PL and CL spectroscopy (CL - where electrons impacting on a luminescent material cause the emission of photons) to map defects in the FhG material with the aim at correlating this to determine minority-carrier lifetimes. Intensive work has been done.

For this task, a purpose-built time resolved PL set-up with a 25 ps resolution has been developed. The luminescent properties of the GIPSOL sample have been determined. They point out a disordered structure with potentially composition variations inducing a slight decrease of the band gap. Life time measurements also confirm the disordered nature of the InGaP layers. Finally, CL spectra have shown different luminescent behaviours depending on the nature and level of doping. The depletion area due to the pn junction is also visible and its length is estimated around 300 nm.

CL spectroscopy has been successfully employed to determine the nature of the radiative transition in heavily doped GaAs layers, to determine the Fermi levels in 2 layers, pointing out a difference of active doping between the substrate and the n-type buffer. Thanks to the models used, the CL can be considered as a quantitative technique to determine active dopant concentration, though the knowledge of the effective mass is critical for the accuracy of the measure. Calibration samples whose dopant concentrations have been determined by electrical measurements could provide reference effective mass values.

CL mappings have been also carried out on the InGaP junction of the TAN sample and highlighted the good homogeneity of the sample at a micrometric scale and the absence of defect areas.

Structural properties and layer thickness

The concentration of Ga, As and P elements in SOL and GIPSOL samples was expected to be quantified with relative uncertainties of up to 15 % using GIXRF techniques and existing tabulated atomic fundamental parameters (net X-ray fluorescence intensity and concentration of the analyte). Complementary measurements based on high resolution X-Ray diffraction (HR XRD) were also planned to determine composition and layer thickness of FhG samples and other III-V samples to be provided by LAAS.

In GIXRF, the incident angle between X-ray beam and sample surface is varied around the critical angle for total external reflection. PTB has developed a reference-free GIXRF which makes the quantification of elemental mass depositions possible without the need for a pre-calibration. Due to the limited availability of samples, Ga and As could not be quantified, as they were matrix elements in the samples provided. Emphasis was therefore put on In and P quantification instead, as they are present in only the window layer for the SOL sample enabling a XRF quantification. The results of the In and P quantification of SOL sample using the different In L-shells are in good agreement with each other. The total experimental uncertainties have been found in the range between 10 % and 15%.

Characterisations by HR XRD have been carried both by PTB and LAAS on SOL and GIPSOL samples and LAAS has extended these characterisations to other samples fabricated by LAAS and based on alloys containing AlGaAs, GaInAs, GaAsN and GaInAsN materials. The elemental compositions and layer thicknesses could be determined with accuracy better than 1 %. In particular, tilting effects have been identified on GaInP based samples. Complementary characterisations were allowing a better evaluation of the thicknesses (see figure 5).

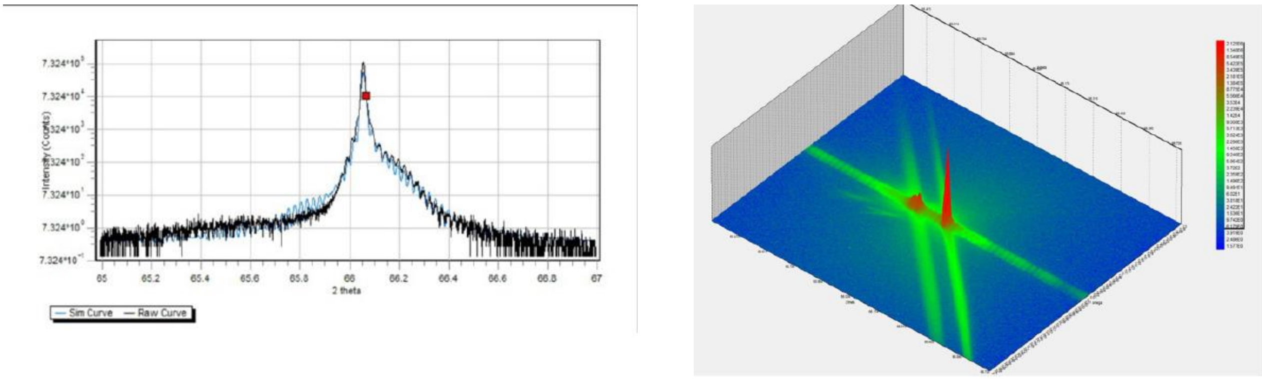


Fig. 5 (Left) HR XRD 2θ/ω diffraction pattern of SOL sample (left) and 2θ/ω mapping of GIPSOL sample (right)

The GIXRF and HR XRD results for a GaInP layer on one SOL sample have been compared and a good agreement has been found:

- Assuming a standard stoichiometry of $Ga_{0.51}In_{0.49}P$ with a standard density of 4.47 g cm^{-3}, these mass depositions correspond to a layer thickness of about 22 nm (using the In results) or 17 nm (using the P result). The discrepancy is due to a deviation in the stoichiometry.
- If using the fitting results of the HR XRD measurements for the $Ga_{0.47}In_{53}P$ layer with a standard density of 4.44 g cm^{-3}), these mass depositions correspond to a total layer thickness of about 21 nm (using the In results) or 17.5 nm (using the P result).

Optical properties

A comprehensive study of optical properties of the multilayer structures of III-V solar cell samples (SOL, GIPSOL and TAN) was jointly carried out at VTT, CEA and LAAS in collaboration with LNE. Spectroscopic ellipsometry and reflectance measurements performed at CEA and LAAS were used to determine the refractive indices, reflection properties of the anti-reflection coating and the thicknesses of the semiconductor layers. The developed methods can be applied in semiconductor manufacturing to analyse the semiconductor layer properties and thus to develop more efficient III-V solar cells.

The results of the gonioreflectometric measurements at VTT showed that the present antireflection coating reduces the reflectance up to 20% at the visible wavelength region. Due to the Brewster's law the reflectance results were mostly analysed for s-polarised light. The incident angle dependence of the reflected light was studied by measuring the reflectance at different angles of incidence light (figure 6). For relative small incident angles between 0° - 40°, the amount of specularly reflected light was less than 25% at visible wavelengths. At incident angles above 40° the reflected light start to dominate over the absorbed light. The effect of the anti-reflection coating was also found to have limited effect on the infrared region where the novel III-V semiconductor based solar cells are also operational.

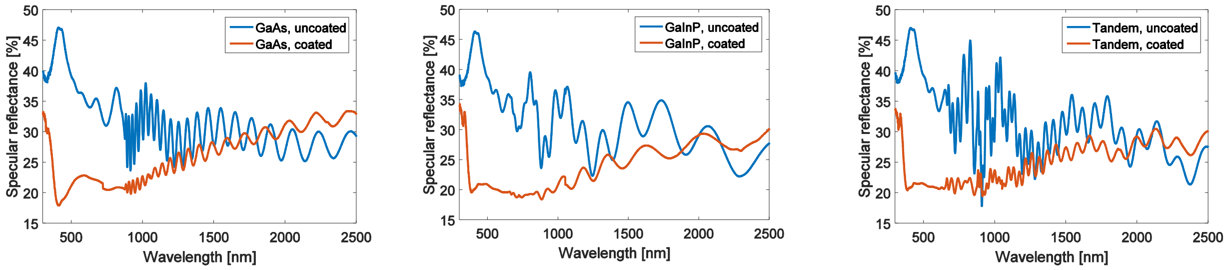


Fig. 6 Specular reflectances of the samples. The angle of the incident light was 10° leading to a specular reflection angle of 20°. The incident light was s-polarised. The results show that the anti-reflection coating reduces the reflectance of the solar cell samples up to 20% at the visible wavelength range between 400-800 nm. At the ultraviolet and infrared wavelengths the effect of the coating is more limited. At the wavelengths above 2 000 nm, the coating cannot reduce the reflectance.

The results of the ellipsometry measurement showed that ellipsometry can be used to study the layer structure of the new III-V solar cells. Ellipsometry is an applicable technique for layer composition determination for solar cells with limited layer complexity. Comparing the layer structure achieved by analysing the ellipsometry measurements with the real layer structure, a good agreement was found.

To get the temperature dependence of the optical constants of layers of solar cells is of high interest. This is indeed very important since multi junction solar cells are likely to be used under sun concentration with adapted Fresnel lenses, raising its operating temperature around 100°C with an efficient cooling system. This increase in temperature affects the optical constants of the used materials and therefore the efficiency of the solar cell. The temperature-dependent optical constants were measured at CEA using spectroscopic ellipsometry on GaAs and AlGaAs samples and the temperature-dependent interband transition energies E1 and E1+Δ were determined and compared to the trends observed from literature. Coherency between the literature and experimental data was found.

Electronic structures

In order to optimise the design of present III-V triple-junction solar cells, the band gap energies of the sub-cells, photocurrent within each cell as well as optimised tunnel-junction between cells need to be determined.

A novel method was developed by VTT to determine the band gap energies of the sub-cells of multi-junction solar cells. The method is based on measuring the emission spectra of the solar cells at different temperatures. Utilising the method requires only a spectroradiometer and a temperature controlled mounting base for the solar cell sample and is thus an easy and low cost alternative compared to other band gap determination methods such as reflectance based techniques.

In addition, several main elements of the present III-V solar cells have been probed by PTB using X-ray absorption fine structure spectroscopy (NEXAFS) in order to reveal any changes of the electronic structure due to the chemical species in which they are present. Deep-level transient spectroscopy (DLTS) has also been carried out at LAAS in collaboration with LNE to investigate the possibility of determining the concentration of electrically active defects in these same samples.

VTT has determined the band gap energy of SOL, GIPSOL and TAN samples by measuring the electroluminescence spectra of these samples at different temperatures (270 – 350 K). Band gap energy strongly depends on the temperature of the p-n junction. However, it can be shown that a temperature independent energy point can be determined from the normalised electroluminescence spectra measured at different temperatures. According to the analysis of the mathematical model of an electroluminescence spectrum of an opto semiconductor, it can be shown that the normalised electroluminescence spectra measured at different temperatures intersects at the band gap energy at 0 K temperature. The novel method developed allows one to determine the wavelength of the band gap energy at an uncertainty of 0.1 nm. Good agreement between the electroluminescence and spectral response was found.

At PTB, the NEXAFS measurements were carried out on SOL, GIPSOL and TAN samples in fluorescence detection mode. For every photon energy a respective fluorescence spectrum was recorded. The net intensities for the relevant fluorescence lines were derived from the fluorescence spectra by deconvolution using detector response functions and relevant background contributions if necessary. The derived line intensities were normalised with respect to the photon energy dependent flux of the beamline. For better comparability, the NEXAFS measurements were also normalised to unity in the high energy region away from the probed absorption edge unless it is stated otherwise.

On GIPSOL samples, no significant differences were observed on the NEXAFS signature of both the Ga-K and Ga-L3 absorption edges by drastically changing Ga-containing species. Both of these findings are in contrast to literature results. Also when comparing the L3-edge NEXAFS at different incident angles of the SOL, TAN and GIPSOL samples, where the Ga-containing species drastically changes, no significant changes in the NEXAFS fine structure can be revealed. This is due to the thick 400 nm GaAs capping layer on these samples, which drastically reduced the sensitivity for the deeper layers.

DLTS measurements have been carried out at LAAS with the assistance of LNE to determine the fundamental electrically active defect parameters caused by metal diffusion in III-V material, and to measure their concentration. Specific samples based on GaAs schottky diodes were jointly designed by LAAS and LNE. They have been fabricated from different MBE growth conditions (temperature, III-V ratio, epitaxial regrowth) then characterised. These DLTS measurements have shown that epitaxial regrowth can create oxygen related deep levels. With optimised growth conditions, the concentration of deep levels in GaAs was too low to be determined by DLTS measurements.

3.2.2 Dilute nitride solar cells

It is expected that MJSC efficiency increases with the increasing number of junctions (a theoretical efficiency of 86.8 % is achievable with an infinite number of band-gaps). As the number of junctions increases the solar spectrum is partitioned into narrower wavelength ranges allowing a better conversion of solar energy. However, as the sensitivity to spectral variations increases with the number of sub-cells, it is important to investigate the possible gain in energy production before a decision is made on the number of sub-cells and the material combination to use. The objective here was to study the properties of a dilute nitride cell, GaInAsN, with band-gap energy of around 1 eV.

LAAS has successfully fabricated GaInAsN test structures (with different In and Sb contents and different doping levels) and GaInAsN single-junction solar cells using molecular beam epitaxy (MBE) growth techniques (figure 7). Prior to this, growth of some calibration samples of GaAsN and GaInAsN layers was necessary to adjust the lattice-match composition on GaAs by MBE. They were characterised by high resolution X-ray diffraction. Some required thermal annealing treatments have been processed on the final GaInAsN samples in order to improve the optical properties.

These solar cells based on GaInAsN materials with a bandgap of 1.16 eV have been distributed to partners for characterisation of optical properties, structural composition, and electronic structures.

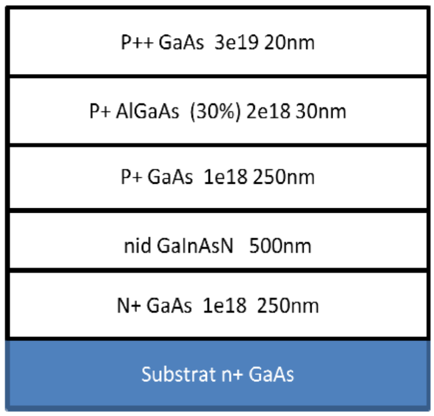


Fig. 7 Nominal layer sequence of GaInNAs based solar cells provided by LAAS.

CEA has used spectroscopic ellipsometry to determine the optical properties and has performed SIMS and Time-of-Flight (TOF) SIMS measurements which have revealed the Si and C doping as well as C segregation at the interface with the substrate for all samples. Si doping level has also been quantified using SIMS. The measurements highlighted In diffusion in the GaAs sublayer and interfacial segregation. PTB has performed Reference free X-Ray Fluorescence on the same sample in order to compare the doping levels with the SIMS results.

To analyse the electronic structure, band-gaps and defects mapping on these test structures, CEA has performed PL measurements on GaInAsN. The temperature study has revealed a S-shape of the GaInAsN peak which is a clue of the good introduction of nitrogen inside the film. The bandgap was derived from the measurements and two features in the electronic structure were observed. They can come from N-clusters or carbon-related defects.

PTB has performed complementary measurements of the electronic structure and for a quantitative depth profiling of dopants using GIXRF. A comparison of the normalised GIXRF fluorescence signal ratio of the N-K and the In-M fluorescence was used to probe the in-depth composition.

Objective 2 Summary

This objective related to the determination of III-V material properties (composition, structural properties, layer thickness, electronic structure and optical properties) was completed successfully. The highlights include:

- *Extensive SIMS composition characterisation of III-V materials completed*. Low energy SIMS techniques with enhanced depth resolution has made possible a quantification of the dopant composition and a characterisation of the quality of interfaces of the dual junction.
- *New III-V calibration samples realised for SIMS techniques*. 12 different III-V calibration samples have been realised and added to the SIMS library of the partners. This will help future quantifications of dopant concentration in III-V materials.
- *Demonstration of complementarity of SIMS and GIXRF techniques*. Using the new III-V calibration samples, a comparison between SIMS and GIXRF techniques between two partners has been

successfully carried out. The complementarity of these two techniques to get accurate dopant profiles in implanted samples has been well demonstrated.

- *Quantitative determination of dopant concentration achieved using Cathodoluminescence (CL) spectroscopy*. CL spectroscopy was found to be a quantitative technique to determine active dopant concentration. The electron effective mass which is a critical quantity for the accuracy of the measurement can be obtained using calibration samples whose dopant concentrations have been determined by electrical measurements.
- *A reference-free GIXRF facility developed at an NMI*. This new capability makes the quantification of elemental mass depositions possible without the need for a pre-calibration. The results of the In and P quantification of SOL sample were found in good agreement with each other and considering the associated uncertainties which have been estimated in the range between 10 % and 15%.
- *A joint and comprehensive study of optical properties of the multilayer structures of III-V solar cell samples achieved*. Spectroscopic ellipsometry and reflectance measurements were used to determine the refractive indices, reflection properties of the anti-reflection coating and the thicknesses of the semiconductor layers. The developed methods can be applied in semiconductor manufacturing to analyze the semiconductor layer properties and thus to develop more efficient III-V solar cells.
- *A novel method developed to determine temperature-invariant band gap energy for III-V opto-semiconductors.* The method has been verified to work with all III-V optosemiconductor compounds. The spectral responsivity and normalised emission spectrum for the GaAs/GaInP solar cell have been obtained.
- *Measured properties of a dilute nitride cell*. Innovative solar cells based on GaInAsN materials with a bandgap of 1.16 eV have been designed, fabricated and distributed to partners which have performed the characterisation of various material properties as planned. For example, optical properties have been determined from spectroscopic ellipsometry based measurements.

3.3 Objective 3: Measuring carrier transport between interfaces in MJSC and characterising narrow tunnel-junction properties

The objective was to better understand tunnel-junction interconnects through the design, fabrication and characterisation of tunnel junctions made with new materials lattice-matched or nearly lattice matched to GaAs. A numerical model had to be established to describe electronic transport in these structures.

For this, it was required to design and fabricate heterostructure based tunnel-junctions with staggered band offset using new materials (GaAsSb and InGaAs) closely lattice-matched to GaAs. The challenge was to produce type III band aligned tunnel junctions with good characteristics by using MBE growth techniques with mixed anions GaAsSb and mixed cations InGaAs to achieve abrupt interfaces. The fabrication and the modelling of this new type of tunnel junction heterostructure is of particular interest not just for reducing the electrical interconnection losses in MJSC, but also for application in the broader scientific and industrial community that employ tunnel junctions in photonics (lasers, VCSEL) and electronics (HBT) devices.

Heterostructures for GaAs-based tunnel junctions

A first extensive experimental study was led at LAAS on the growth conditions to achieve high peak current in GaAs-based tunnel junctions. The effects of different physical parameters (dopant species [Si for N and Be and C for P-doping], doping levels, layer thicknesses, special growth conditions to maximise the doping level, operating temperature). The doping levels were determined by Hall effect measurements at LAAS, by SIMS and infrared ellipsometry in collaboration with CEA, and by infrared reflectivity in collaboration with Institut d'Électronique et des Systèmes (IES) at the University of Montpellier. These samples and experimental data have served as basis for the modelling study reported below.

Development of type II staggered band offset TJ

The type II so called staggered band heterostructures are inherently very advantageous to enhance the tunneling mechanisms, and then this solution is very beneficial to decrease the serial resistance while increased the achievable peak current. LAAS has investigated the heterostructures formed by GaAsSb and InGaAs which can be grown on GaAs lattice, and with which the band offset presents a type II configuration.

Also several parameters are important to study: the In and Sb composition in the alloys that reduce the bandgap of the materials, and the doping levels. The effect of layer thicknesses has also been studied knowing that these alloys are strained on GaAs and can be relaxed above a certain critical thickness.

LAAS has achieved an optimal type II GaAsSb/InGaAs tunnel junction structure presenting a peak current as high as 1300 A/cm^{-2}, value which equals the best results obtained on TJ grown on GaAs.

GaAsSb/InGaAs type II tunnel junction has also been investigated by LAAS to check the impact of alloy compositions and doping levels. TJ samples were grown by MBE with Sb and In compositions of 5 and 10% with different doping levels (N = 4.5 10^{18} to 1.3 10^{19} cm^{-3}, P = 3 10^{19} to 10^{20} cm^{-3}) and thicknesses (7/7 nm, 15/15 nm, 50/50 nm). Current densities as high as 320 A/cm^2 were measured, but the effective peak current density through the device was certainly higher than this value as our process was not adapted to measure such high current density.

Another solution that has been tested is the incorporation of a thin quantum well formed by a low bandgap material within a GaAs tunnel junction. It has been successfully demonstrated that this approach increases the peak current with a factor of 43 (30 A/cm^2) compared to GaAs standard TJ. The result of this study is highly innovative compared to the state-of-the-art, and the achieved results demonstrate the high potential of this approach.

Electronic transport modelling in tunnel junctions

A significant work on the theory of transport mechanisms in tunnel junctions has been undertaken. This theoretical modelling work, which has been quantitatively compared to experimental data, was essential to understand and simulate the transport mechanisms in tunnel junction structures. Initial simulations using Silvaco Atlas software has shown that the Band-to-Band Tunnelling (BBT) model needs to be calibrated to match the experimental data. This indicates either that the model is not accurate enough to perform quantitative simulations or that the BBT mechanism is not the predominant one in GaAs tunnel junctions. Other tunnelling mechanisms, such as Trap-Assisted-Tunnelling, could thus dominate the carriers transport in the device. A fully analytical BBT physical model has been completely built and programmed with the open-source program “Scilab. It indicates that BBT is perfectly able to describe the carriers transport in the tunnelling device, if the complex band structure of GaAs is accurately considered. In order to validate this model, the simulations results have been compared to experimental data obtained from standard GaAs-homojunction-based tunnel junctions fabricated by LAAS. This first implementation led to very good agreement between the modelling results and the experimental I-V curves, however by being restricted to moderately doped tunnel junctions.

In a second refining step, the impact of multiband corrections has been investigated on the current density of GaAs Tunnel Junctions (TJs) calculated with a refined yet simple Semi-Classical Interband Tunneling Model (SCITM). The non-parabolicity of the considered bands and the spin-orbit effects are considered by using a recently revisited SCITM available in the literature. The model is confronted to experimental results from a series of MBE grown GaAs TJs and to numerical results obtained with a full quantum model based on the Non-Equilibrium Green’s Functions (NEGF) formalism and a 6-band k.p Hamiltonian (figure 8). It must be pointed out the importance of considering the non-parabolicity of the conduction band by two different measurements of the energy-dependent electron effective mass in n-doped GaAs. An innovative method has been proposed to compute the non-uniform electric field in the TJ for the SCITM simulations, which is of prime importance for a successful operation of the model. It has been demonstrated that, when considering the multiband corrections and this new computation of the non-uniform electric field, the SCITM succeeds in predicting the electrical characteristics of GaAs TJs, and are also in agreement with the quantum model. Beside the fundamental study of the tunnelling phenomenon in TJs, the main benefit of this SCITM is it can be easily embedded into drift-diffusion software, which is the most widely-used simulation tool for electronic and opto-electronic devices such as Multi-Junction Solar Cells (MJSCs), Tunnel Field-Effect Transistors (TFETs) or Vertical Cavity Surface Emitting Lasers (VCSELs). This last study has been led in a close collaboration between the LAAS and the Institute of Materials Microelectronics Nanosciences De Provence (IM2NP) in Marseille (expert in quantum modelling), and also for the experimental measurements with the IES, the CEA and the LNE.

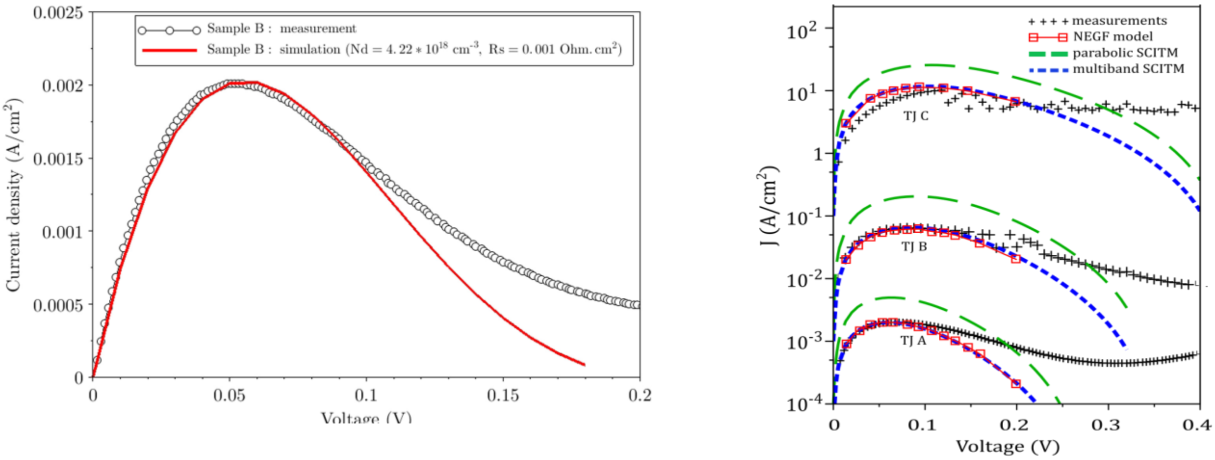


Fig. 8 Experimental J-V characteristics compared to the simple BBT analytical model (Left), and the refined semi-classical and NEGF simulations for different tunnel junctions.

Objective 3 Summary

The works aimed at better understanding tunnel-junction interconnects have been successfully carried out, yielding the following highlights:

- *New tunnel-junction samples fabricated and tested*. Based on numerical simulations of tunnel junctions, a new design was developed showing the feasibility of peak current up to 1300 A/cm^2 which reaches the best results obtained on tunnel junction grown on GaAs. Following this study, several samples were fabricated by MBE then tested. Current densities as high as 320 A/cm^2 were measured.
- *New numerical modelling developed to better understand the transport in tunnel junctions.* A reliable analytic model for predicting quantum band-to-band tunnelling has been developed. It has been demonstrated that non-local band-to-band tunnelling model is able to quantify satisfactorily different experimental current-voltage I-V measurements, taken on different tunnel junction samples with various doping levels, showing current peaks up to 10 A/cm^2.
- *Extensive numerical simulations carried out on different types of tunnel junction structures.* The band structure modification due to the high doping was highlighted and its effect of the tunnel mechanism was quantitatively evaluated. The improved simple model was confirmed and shows good agreement both with experimental measurements and with a full quantum model developed by Institute of Materials Microelectronics Nanosciences De Provence (IM2NP) in Marseille, France, part of project partner CNRS.

3.4 Objective 4: Development of reliable tools and workflows to measure size dependent electronic structures of nanostructured semiconductor quantum dots

The photovoltaic industry can gain significant advantage in using nanostructured materials to meet the requirements for the next generation solar cells in terms of high efficiencies and lower cost. In these systems thermalisation losses could be reduced by the use of quantum confined semiconductor structures such as Si, Ge, InAs or GaAs. The band-gap of the quantum dots (QDs) is controlled by the size of the dots through the quantum confinement phenomenon. When coupled to a conventional or MJSC cell, such a gap engineered cell could theoretically lead to a high efficiency. This objective was mainly focused on the development of reliable tools to detect QDs and to determine the relationship between the size of the QDs and of the band-gap.

For PV applications the QDs have to be deposited as layers. LAAS has prepared free-standing QDs nanostructures of InAs using MBE without optimisation on size and density and has subsequently deposited them on a substrate of GaAs. This technique has the advantage that the layers can be constituted exclusively from the QDs. Their properties depend on many factors such as surface energy, substrate temperature, flux ratio, and growth rate.

InAs-based QD samples grown on GaAs have then been fabricated at LAAS (figure 9).

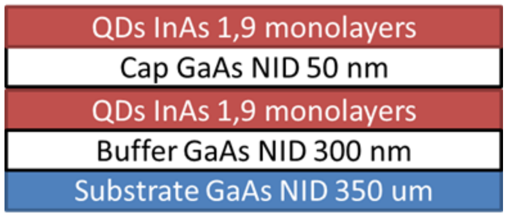


Fig. 9 Structure including self-assembled InAs quantum dots grown by MBE at LAAS.

The measurement of charge carrier density and dopant mapping of QDs structures determined using Scanning Microwave Microscope (SMM) was found by the consortium to be extremely challenging. The project has then focused on only the detection of QDs. Prior to observe quantum dots (QD) by SMM in these samples, measurements using AFM in tapping mode have allowed one to detect them. The surface density of QDs and their approximate sizes have been determined.

Densities of three of these samples have then been measured at LNE using AFM. Various values were found, in the order of 10 entities/µm^2, 400 entities/µm^2 and 680 entities/µm^2. The size of the QDs was approximatively 5 nm for the three samples (figure 10).

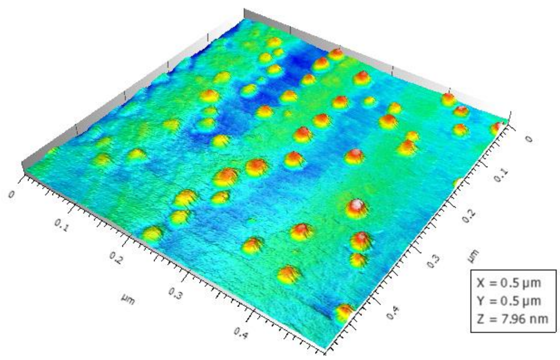


Fig. 10 AFM 3D view of Quantum Dots sample grown by MBE at LAAS.

The detection of QDs was finally found not possible with SMM. However, the feasibility of the electrical detection of QDs by using a Resiscope system which is another electrical Scanning Probe Microscopy (eSPM) techniques has been demonstrated in the frame work of a collaboration with the Génie électrique et électronique de Paris (GEEPS) in Gif sur Yvette, France, part of project partner CNRS (figure 11).

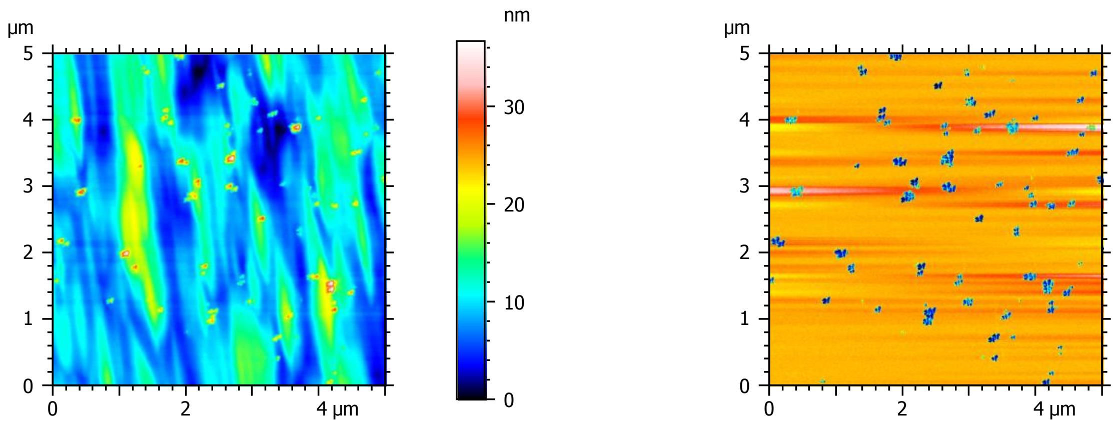


Fig. 11 (left) topography and (right) current image of one QD sample measured using a resiscope.

Furthermore structural properties of the QDs have been investigated by CEA and PTB.

CEA has carried out X-Ray Photoelectron Spectroscopy (XPS) measurements to determine the degree of oxidation then to obtain the value of the Fermi level. PL and CL measurements have also been carried out at CEA to resolve the electrical activity of individual grains and quantum confinement effects through correlated CL and PL spectroscopy. The different contributions in the XPS spectra (In, As, Ga, C and O) have been compared between the samples. The XPS spectra are calibrated using the carbon peak. A same behaviour has been found for the two samples. In and As signals are enhanced for the sample with the higher QDs density, as expected. XPS measurements have allowed one to calculate the degree of oxidation. The ratio between the Ga oxide contained in the GaAs cap and bulk components was found nearly identical for the two samples while the oxidation of In, related to the oxidation of the surface of the InAs quantum dots was found lower for the sample of lower QDs density, as expected. Finally the XPS spectra around the valence band have shown the same form and energy level of valence band for both samples.

PL and CL measurements have been found consistent with the expected QD density, but they have also revealed differences between the samples. For the higher density sample, a gaussian emission peak is observed and attributed to the normal distribution of the QDs sizes. On the contrary for the lower density sample, the emission is broad with lot of small peaks which can be due to the emission of single QDs under the measurement spot.

In complementary way, PTB has used the NEXAFS and GIXRF technique to determine both the electronic and the compositional structures of the QD samples. The GIXRF measurements clearly revealed the surface and the buried QD layers and thus allowed for a distinct analysis using NEXAFS. The NEXAFS measurements have thus been performed at two different incident angles for both the In-L3 absorption edge and the In-L2 absorption edge. The shallow angle probes mainly the surface QD layer whereas the steep angle probes both QD layers. This variation would thus reveal any significant chemical deviations between the surface QDs and the buried QDs. For both edges, there is no significant difference for the two incident angles. Thus, in terms of the methods sensitivity, both probed QD layers were chemically and electronically equal.

Objective 4 Summary

The measurement of charge carrier density and dopant mapping of quantum dot structures determined using SMM was found by the consortium to be extremely challenging. The objective has then focused on only the detection of quantum dots. The key results achieved are:

- *Free-standing InAs QD nanostructure samples fabricated*. Several free-standing InAs QD samples were prepared by MBE and deposited on a GaAs substrate. Prior to observing quantum dots by SMM in these samples, measurements using AFM in tapping mode have allowed one to detect them. The density of quantum dots and their approximate sizes have been successfully determined.
- *Successful detection of QDs using a Resiscope.* The detection of QDs was finally found not possible with SMM. However, the feasibility of the electrical detection of quantum dots by using a Resiscope system which is another electrical Scanning Probe Microscopy technique has been demonstrated in the frame work of a collaboration with the Génie électrique et électronique de Paris (GEEPS) in Gif sur Yvette, France, part of project partner CNRS.
- *Structural properties of the QDs investigated.* XPS measurements performed on these QD samples have allowed the degree of oxidation to be calculated. PL and CL measurements are consistent with the expected quantum dot density, showing discrete spectral features for the low density sample and a gaussian emission for the high density sample.

3.5 Objective 5: Measuring thermoelectric properties of III-V material and thermal transport across interfaces

This objective was to develop measurement methods to determine thermal transport properties of complex III-V multi-junction structures that have more than 3J or that use the thermoelectric effect to improve the overall efficiency of the solar cell. This objective included the study of the potential theoretical tools useful to model the thermal properties in MJSCs by investigating any potential thermal gradient within the system and the possibility to harvest this gradient to enhance the performance of the system through its thermoelectric properties.

A new facility to measure the thermal conductance of solar cells and related wafers with more accuracy has been developed at NPL. Results demonstrate the importance of thermal contact resistance. The impact of sample mounting and testing procedures on the precision of thermoelectric module measurement was also studied. For the first time, the variability in the electrical output due to mechanical pressure or type of thermal interface materials was quantified. Further to this, the contribution of the temperature difference and the mean temperature to the variation in the output performance was quantified. In addition NPL mounted a noise spectroscopy measurement set-up based on a rig to measure electronic noise in sample as a function of temperature. However, the precision of the set-up was found relatively poor and the temperature can only be measured with an uncertainty of about 10% at room temperature. This is not sufficient to observe potential thermal effect in MJSC and this approach has not been pursued.

NPL has investigated a number of models that have been implemented as Python codes. At first, a “complete” thermal model has been considered, involving classical phonon transport and able to include hot carrier effects and thermoelectric exchange of energy. Modelling of semiconductor devices is usually done with drift-diffusion models. The main assumptions of these models are: (1) thermal equilibrium between the lattice and the charge carriers and (2) electron and hole populations have their own characteristic Fermi level and temperature. The depletion region approximation is also widely used. These approximations give a good understanding of the physical processes involved in PN junction semiconductor devices under many circumstances. However, these assumptions are not valid in the presence of “hot electrons” in solar cells or in the presence of thermoelectric effects.

A more complex model, able to represent both cases is to consider hydrodynamic flow for the electron and hole population. This model can only be solved analytically and while an improvement of the total efficiency of a module by a few percent maybe possible it would require some sort of energy filtering from the external junction of the devices. It is found not possible with the current technology and consequently the investigation was stopped in this direction.

Another model has been investigated at NPL and relies on the 3ω method which is used frequently to measure the thermal conductivity of thin films: An electrically conductive pattern is deposited on the sample. An AC current with frequency ω is driven through the pattern causing Joule heating at a frequency of 2ω. The generated thermal wave diffuses into the sample and the penetration depth is determined by the thermal diffusivity of the specimen and the frequency of the AC current. Since the resistance of the heater is proportional to the temperature, the resistance will be modulated at 2ω. The voltage drop along the test structure contains therefore a third harmonic that depends on the AC temperature rise of the heater. This is used to extract the thermal conductivity of the sample. Thermal conductivities of thin films down to several nanometers thickness were measured using this technique.

The accuracy of the thermal conductivity measurement is in large part determined by the heat conduction models. An approximate analytical expression is often employed to determine the thermal conductivity of from the slope of the real part of the AC temperature expressed as a function of the logarithm of modulation frequency. The corresponding temperature drop developed in the substrate may be then calculated. For measuring the thermal conductivity of a thin-film deposited onto the substrate, the temperature drop across the thin film is inferred from the difference between the measured total temperature rise and the calculated temperature drop across the substrate. Using a simple one-dimensional heat conduction analysis, the thermal conductivity of the thin film can be determined.

Objective 5 Summary

The highlights of this completed objective are the following:

- *New measurement capabilities at an NMI*. A new facility to measure the thermal conductance of solar cells and related wafers with more accuracy has been developed. Results demonstrate the key importance of thermal contact resistance.
- *First metrological study of the impact of mounting and testing procedures on the precision of thermoelectric modules measurement*. Variability in the electrical output due to mechanical pressure or type of thermal interface materials has been quantified for the first time. The respective contribution of the temperature difference and the mean temperature to the variation in the output performance has been quantified.
- *Developed model to describe thermal transport between the layers of III-V MJSC*. Based on the available data for thermal conductivity of the different materials, it was predicted that no significant thermoelectric energy recovery would be possible in the MJSC.

3.6 Objective 6: Development of traceable and reliable calibration methods, and standards for determining device efficiency, linearity, temperature dependence and spectral responsivity of MJSC device

The overall objective here was to establish traceable and reliable laboratory calibration methods for III-V multi-junction solar cells around Europe. Creating standards for the determination of the devices' short circuit current as well as power conversion efficiency is crucial since stakeholders need such certifications to enable new MJSC products to enter the market. So far, only MJSC with a maximum of three active layers (3J) can be calibrated in NMIs/DIs across Europe and the devices are measured in solar simulators and traced to reference cells which are calibrated directly to the sun's spectrum at Air Mass zero (AM 0) during balloon flights. Under such realistic and consequently non-controllable conditions a lower calibration reproducibility and a higher uncertainty is likely compared to primary calibrated reference samples investigated e.g. by differential spectral responsivity (DSR). In addition to reducing the uncertainty, there is a need to extend the calibration methods to enable measurements on MJSC with more than three junctions to meet industry's needs in this area. To achieve this objective, four main tasks were completed:

- Evaluation of the MJSC devices delivered by AZUR SPACE;
- Development and construction of additional measurement instrumentation components for DSR setup;
- Extension of measurement facilities to perform multi-junction solar cell calibrations;
- Establishment of a multi-junction solar cell calibration standard.

3.6.1 Evaluation of the MJSC devices delivered by AZUR SPACE

The first part of the objective was to evaluate MJSC (complete solar cells consisting of multiple stacked active layers) as well as component cells (comp. cells, which are cells corresponding to MJSC but with all but one active layer deactivated) fabricated by AZUR SPACE and to be used as reference cells by the project partners. The comparability of the measurements performed by the partners requires agreement upon the contacting and measurement methods as well as procedures to ensure uniform data evaluation.

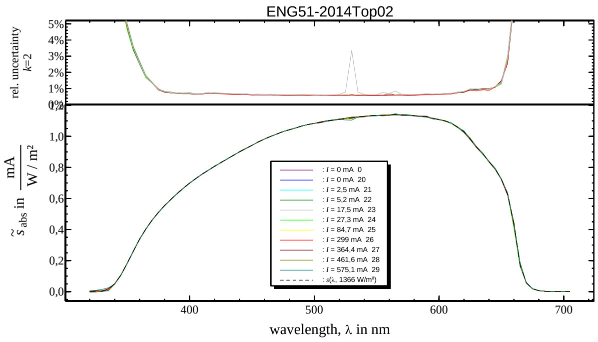
The second part was to calibrate the photocurrent of comp. cells test samples under standard test conditions using solar simulators and differential spectral response for use as references during the project. Until now solar cell calibrations with an uncertainty of 0.5 % have only been possible on Si reference solar cells while for component cells the achieved uncertainty is 1 %. By performing comp. cells calibrations using Laser-DSR, the measurement uncertainty was expected to reach 0.5 % or lower. An in-depth investigation of the dependence of the open circuit voltage (V_{oc}) on temperature and irradiance was required since this parameter is crucial for the calibration of multi-junction solar cells.

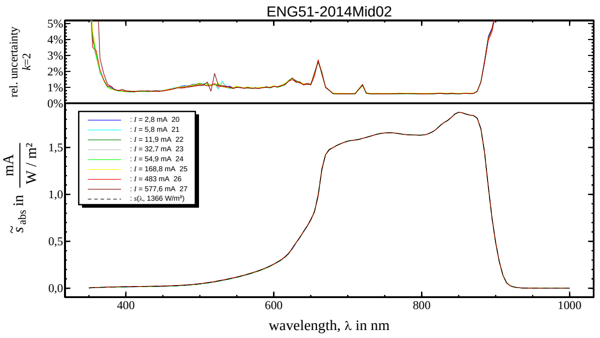
AZUR SPACE fabricated three sets consisting of component solar cell assemblies as well as corresponding triple junction solar cell assemblies. A solar cell assembly (SCA) consists of the solar cell, a 300 µm thick front glass as well as interconnectors. These cells lead to the necessity of developing a complete housing to perform reproducible measurements at INTA and PTB. The SCAs have then been equipped at PTB with a temperature control sensor as well as cell holder and sockets.

To determine the short circuit current under defined testing conditions PTB uses the differential spectral responsivity (DSR) measurement method. Here the device under test (DUT) is illuminated on the one hand by modulated monochromatic light and on the other hand by white bias light. The modulated part is used to calibrate the spectral responsivity (photo generated current per irradiance per wavelength) of the DUT against a primarily calibrated irradiance standard. The bias light is necessary to determine any nonlinear relations between the overall irradiance and the photo current. These measurements are performed at different bias irradiance levels from which the actual spectral responsivity under testing conditions is calculated. From this and the given standard spectrum the short circuit current of the cell is determined.

The Laser DSR setup of PTB (L-DSR) allows one to calibrate World Photovoltaique Scale (WPVS) reference solar cells photo current under standard testing conditions with an uncertainty below 0.5%. Such references consist commonly out of crystalline silicon so that the setup was optimised so far in a spectral range from 280 nm up to 1200 nm. To be able to calibrate solar cells with a photo response above 1200 nm the laser based monochromatic system had to be adjusted for optimum homogeneity as well as output power. Due to a system design flaw the laser system lacks output power between 1615 nm to 1700nm. To overcome this limitation measures have been taken.

The two sets of component cells delivered by AZUR SPACE and housed by PTB were measured. All cells consisted of a complete stack typical for multi junction solar cells, *e.g.* an InGaP top junction, an InGaAs middle junction and a Ge bottom junction (figure 12). In each component cell only a single junction is electrically contacted and therefore active. Each cell was measured at eight different bias levels between ~ 0 and ~ 1400 W/m^2 irradiance. Top and Middle component cells were traced to a calibrated silicon photo diode, while the germanium cell was traced to a calibrated germanium photo diode. The germanium component cells were measured additionally at the DSR facility at 5 different bias levels to determine the spectral response between 1600 nm and 1700 nm. From the spectral responsivity the photo current under AM0 as well as AM1.5 conditions and at 25°C was determined. The measurement uncertainty budget for both measurement setups has been established. The overall uncertainty was determined by Monte-Carlo simulations. The targeted uncertainty of 0.5% was achieved for top and middle cells, while the uncertainty of the bottom cells is at about 1%. The larger uncertainty in bottom cell calibration in comparison with the top and middle cells originates from multiple sources. First top and middle cells and the reference are measured at the same amplifier setting to cancel out amplifier related uncertainties. Due to the large short circuit current at 1300W/m^2 of the bottom cells different amplifier levels had to be used so that a direct calibration of the amplifiers was necessary. This leads to an additional uncertainty source. Secondly performing the calibration at two different setups with different properties introduced further uncertainties so that here only a relative uncertainty of approximately 1% could be reached.





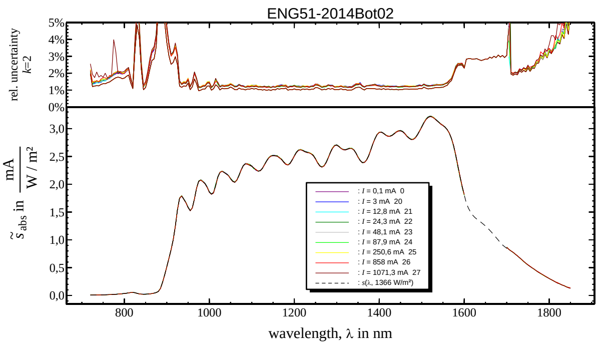


Fig. 12 Differential responsivity at multiple bias levels (solid lines) and AM0 condition (dashed line, in case of the bottom cell) including simulated uncertainty for: top (top-left), middle (top-right) and bottom (bottom-right) comp. cells.

For its counterpart, INTA has calibrated two complete sets of AZUR SPACE comp. solar cells. The calibration has been performed following the ordinary procedures based on ISO 15387 standard. Firstly INTA used one single source AM0 close matched solar simulator to gather the short-circuit current *I*sc of the comp. solar cells Top, Middle and Bottom. This implies a previous measurement of their relative spectral response and the corresponding assessment of the mismatch factor. INTA calibrated a set of single component reference cells (SCRC) in 2011 with traceability to a set of CASOLBA Balloon Flight primary standards that belongs to AZUR SPACE and used them as reference cells for the calibrations. INTA adjusted the spectra of one of the triple source solar simulators in the laboratory using the above-mentioned values of SCRC's *I*sc at AM0 conditions. In these conditions, INTA obtained the calibrated values of the corresponding triple junction solar cell.

An in-depth investigation of the dependence of the open circuit voltage (V_{oc}) on temperature and irradiance had to be performed since this parameter is crucial for the calibration of multi-junction solar cells. INTA has measured the V_{oc} temperature dependence of comp. cells in the range of temperatures from 20°C to 65°C. The temperature coefficient values were found in the range of – 2 mV/K with a standard uncertainty of a few mV/K.

INTA has also determined the mismatch and uniformity factors for data evaluation since both of which are necessary to correctly determine the short circuit current of MJSC under standard test conditions. Indeed, when a solar cell calibration is performed under a steady state solar simulator using a primary standard or secondary standard with traceable calibration value, the standards state that the correction due to the mismatch factor must be introduced. It takes into account the differences in terms of spectral response in both reference and calibration solar cell. It also takes into account the differences in terms of spectrum between the tabulated AM0 (or required spectrum) and the one that the solar simulator is generating. However, there is an additional source of error and hence, uncertainty, that arises from the non-uniformity of the solar simulator light beam at the working plane and that is not included in the standards. Once it is defined, a corresponding uniformity factor (C_{UF}) must be introduced in the equation for the I_{sc} calibration in order to correct for the real value. This mentioned uniformity factor has also a contribution on the uncertainty that laboratories for solar cells calibrations should control and introduce in their calculations and associated reports. Here the C_{UF} value was equal 1 and its uncertainty contribution was found negligible at the moment of performing the uncertainty budget.

3.6.2 Development and construction of additional measurement instrumentation components for DSR setup

A typical DSR setup to measure MJSCs against photodiodes consists of a modulated broadband tuneable light source, a sample holder with a variable temperature system, halogen bias lamps as well as monochromatic bias light adjusted to the band-gaps of the single component cells and electronics to perform DSR measurements with bias voltages.

Before calibrating MJSC devices, the spectrally resolved homogeneity of the illumination from the monochromatic bias lamps needs to be characterised. The measurement uncertainty of TUBITAK's DSR setup has been determined by performing reference calibrations on single junction solar cells. Procedures for short circuit current measurements with DSR have then to be developed as a calibration standard routine. After completing the development of the LED sun simulator, calibrations have been performed and validated on 3J MJSC as well as on four-junction (4J) solar cells. Finally, the DSR setup capabilities have been assessed by measuring the characteristics of the same MJSC samples at INTA, PTB and TUBITAK. This comparison has focused on the establishment of unified procedures, sample evaluations and documentation in addition to the measurement uncertainty.

To calibrate MJSCs *via* DSR measurements voltage and monochromatic irradiance bias are necessary. Although the first is directly accessible with the used transimpedance amplifier, for the latter monochromatic bias towers have to be designed and constructed.

Three monochromatic bias towers for MJSC calibrations were constructed by TUBITAK in cooperation with PTB. During testing it was found out, that two LED Bias towers are sufficient to provide enough irradiation for the intended purpose. Also it was decided that halogen light sources are sufficient to saturate the Germanium bottom cells so that no IR-LEDs above 800nm very implemented.

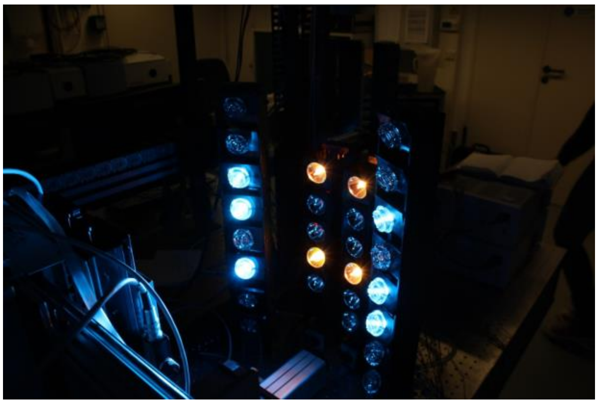


Fig. 13 Bias lights working at AM0 like conditions.

The DSR system developed by TUBITAK has a Xe light source equipped with AM1.5 used as a bias light, a QTH (quartz tungsten halogen) and a UV enhanced Xe light sources which can be supported by Ceramic IR element for generating probe light (tuneable light source) at the output slit of the monochromator (figure 14).

In order to direct the bias light onto the surface of the solar cell a fiber bundle was used as a light guide component. The system is fitted with two trans-impedance amplifiers used to determine *I*sc of the MJSCs and to monitor photocurrent of Si and InGaAs photodiodes used for compensating the time drift of the probe light. The averaged photocurrent and relative deviation on the probe light are first determined for a time interval of 60 sec for any wavelength then the simple and proportional subtraction process is being applied to the averaged photocurrent induced by probe light. The optical power levels of the monochromatic probe light extending from 260 nm to 1100 nm wavelength range vary from 1 µW to 5 µW for the spot size ranging from 2 mm to 5 mm.

Fig. 14 DSR System established at TUBITAK for calibrating solar cells.

To extend the reflectance measurement capability for MJSC up to 2 µm, VTT has developed two different gonioreflectometric setups. The first setup is based on a commercial Agilent Cary 7000 gonioreflectometer with appropriate software. The other setup is built by using discrete components, such as monochromators and photo detectors. In addition to solar cell reflectance measurements, the developed devices can be used in various applications requiring high precision reflectance data, such as different kind thin film structures. Current-to-voltage converter (CVC) is required to read the signals from the sensors of such a gonioreflectometer. However the market has a lack of CVC which meets the requirements of high gain, low noise, high accuracy, stability, and traceability. VTT has then developed a new CVC, which meets these requirements to carry out gonioreflectometric measurements on a metrological level. The device is capable of amplifying the low current signal of the sensor from 10^3 up to 10^{11}.

PTB has constructed Ulbricht Sphere based optics and housings for a LED based solar simulator involving the monochromatic BIAS light towers developed during the project and allowing PTB, TUBITAK and VTT to calibrate MJSC devices with more than three junctions. Basically, the idea is to generate a spectrally homogeneously mixed light field where each sub-junction of a MJSC device can be controlled individually.

70 individual LEDs are placed in 14 groups onto single water cooled cylindric LED base. For of such cylinders in a first prototype are mounted to an Ulbricht sphere with a barium sulfite surface treatment and a diameter of 500mm (figure15). In the center of the four cylinders the central light output port is positioned. Direct light from LEDs are blocked with additional shutters within the sphere. To generate light in the wavelength regime above 1000 nm a water cooled, gold plated aluminum cylinder with an integrated 1000 W FEL halogen lamp is used. To monitor the light field two additional ports one for a Photodiode and one for fiber optics in connection with an array spectroradiometer are applied. The spectral homogeneity was found to be better than 0.5%.

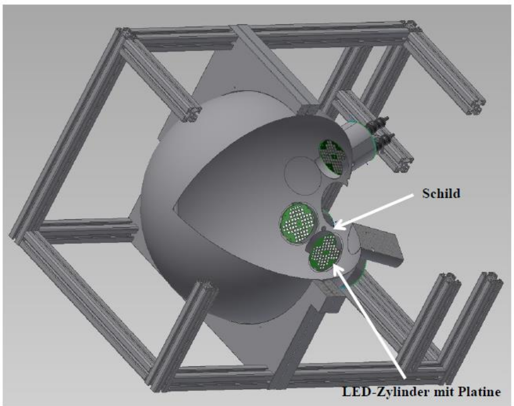


Fig.15 Construction plan of the Ulbricht Sphere.

It was also necessary to develop the power control electronics and software for the LED based solar simulator. Adjustable constant current power supplies were developed at PTB to control the absolute irradiance output of each group of LEDs. Generally, the power supply supports 64 LED groups with a maximum DC voltage rating of 40V. In the current prototype system 56 individual LED groups are available. The constant current can be adjusted in 0.5mA steps and a group of 16 LED channels can be adjusted with one software command. The current stability of the power supply as well as the time stability of the LEDs allow an application without active current control after adjustment after adjustment of the correct LED output spectrum. For controlling the solar simulator a multi-mode Labview based software was developed which interact during runtime with a python script for spectral adjustments. In detail the LabVIEW program is responsible for hardware control (*e.g.* current settings as well as spectral readings of the monitor array spectroradiometer). In the automatic adjustment mode, the current SoSi spectral composition is sent to the python script which checks for deviations from the target spectrum and returns adjusted output current values for the LED groups. The LabVIEW program subsequently sets these new current values and the control loop starts from the beginning. After a sufficient spectral match between target and actual spectrum is reached, the control loop is switched off and the solar cells are measured at these fixed values. For irradiance variation all LED channels can be linearly altered so that no additional control loop run is necessary. For the adjustments with component cells for MJSC calibrations individual spectral ranges in the spectrum can be linearly altered individually.

3.6.3 Extension of measurement facilities to perform multi-junction solar cell calibrations

The activities reported here aimed at implementing the additional instrumentation developed in the task (described in 3.6.2) into the final setups for test and validation of MJSC.

PTB has incorporated the monochromatic bias light towers constructed in the project into the existing Laser-DSR setup. Additionally a voltage source to apply a dc bias voltage to the device under test was used. A method for a synthetic short circuit current calibration of MJSC in laboratory test conditions has been established (figure 16).

The method relies on procedures reported in literature and are commonly used in the community to determine the spectral responsivity of MJSC. Since the sub-junctions of a MJSC are connected in series, it is not possible to measure a single junction directly with the standard DSR method. To overcome this limitation, monochromatic bias lights (“blue”LEDs at 430nm for top junction, “red” LEDs at 780nm for middle Junction and halogen sources for bottom Junction) are used. The center wavelength of these light sources is chosen so that they mainly generate charge carriers in a single junction. Now these lights are tuned so that the current of one junction limits the overall solar cell current. Now this limiting junction can be measured via DSR.

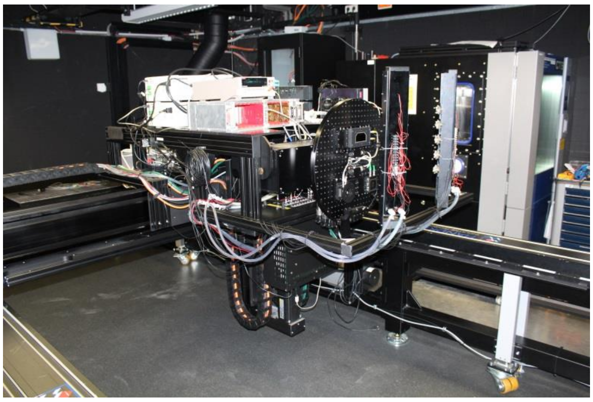


Fig.16 PTB laser DSR set-up fitted with amplifiers, dc voltage source and LED Bias towers.

Test measurements were performed to find correct parameters for calibration. Laser-DSR calibration was performed and data evaluated. Differential spectral responsivity for all three sub cells of a MJSC was obtained and measurement uncertainty of 2% for I_{SC} of MJSC under AM0 conditions (k = 2) was achieved.

TUBITAK assembled and tested its DSR setup incorporating the developed monochromatic bias light towers. The set-up was fitted with a revised DC voltage bias circuit and new DC light bias composed of wide viewing and extremely high output power LED illuminators with peak wavelengths of 470 nm, 750 nm and 1300 nm. Each LED illuminator is fixed on a supplied heat sink and a power supply was designed to supply a required power to each LED illuminator individually. DSR calibrations of comp. solar cells and MJSCs have then been performed with expanded uncertainties (k = 2) ranging from 2.29 % to 12 %.

Once the extension of PTB and TUBITAK systems were completed, three different comparisons have been performed between PTB, TUBITAK and INTA:

- A first comparison has been undertaken between spectral responsivity experiments considering that only the PTB investigations were meant as absolute calibrations at AM0 conditions. The results from INTA and TUBITAK are targeted at relative corrections due to spectral miss match effects during solar simulator calibrations. An absolute comparison of these results is difficult since the latter measurements are traced to radiative power standards while the PTB measurement is traced to an irradiance standard. This leads to a further uncertainty component due to the necessary cell area determination. Anyhow even with these limitations all results show good relative matches, partly even on the absolute scale.

- The second comparison dealt with the IV-characteristics measurement of a triple junction solar cell via LED based Solar Simulator at PTB and a triple source solar simulator of INTA. Even though the LED based system show a relatively high measurement uncertainty due to inhomogeneity as well as a broad angular distribution of the light field, a good match between the measurements was reached.
- A final comparison between the three labs has been carried out on photo currents. Even though for the bottom junction component cell larger deviations were found, for the multi junction as well as the current limiting top and middle component cells good agreements were obtained. Since the solar simulator calibrations were only traced to secondary working standards, a direct comparison to balloon flight calibrated cells is found necessary in the future to further investigate the comparability of these calibration methods.

Beside, PTB has calibrated quadruple junction solar cells using LED-based solar simulator against calibrated single junction solar cells under AM0 condition. The obtained results demonstrate the suitability of such a solar simulator for quadruple junction MJSC calibrations.

Unified calibration procedures and measurement uncertainty budgets have been jointly derived by INTA, PTB and TUBITAK from the performed experiments. Unified procedures were drawn up on primary component cell DSR calibration, solar simulator calibration and relative DSR measurements.

3.6.4 Establishment of a multi-junction solar cell calibration standard

The objective here was to gain further insight into the parameters influencing the calibration of MJSC and to transfer this knowledge from the NMIs/DIs to the stakeholders.

The unified calibration procedures mentioned above were included in a good practice guide on multi junction reference solar cell calibration methods. This good practice guide on “Calibrations of Multi Junction Solar Cell and Their Respective Reference Devices” shaped by INTA, PTB and TUBITAK has been distributed to partners and stakeholders.

Based on this good practice guide, a pre standard report on MJSC calibrations according to ISO/IEC draft 60904:8-1 has been written by PTB. Indeed, at PTB using laser based DSR measurement facility, it was tested if the instructions given in the ISO/IEC 60904:8-1 draft are sufficient to determine the short circuit current at AM0 conditions of commercial MJSC devices. From the obtained results, PTB was able to make recommendations to support the standardisation process of ISO/IEC 60904:8-1. The ISO/IEC 60904:8-1 draft was found very good to determine the spectral responsivity of MJSC reliably. Furthermore it is possible with suitable samples to determine the I_{AM0} of the limiting junction even without detailed knowledge of the IV-characteristics of the sub junctions. Finally with the method presented by Siefer et al even a DSR correction of sub junctions influenced by small parallel resistance is possible and an absolute spectral responsivity of this junction can be determined.

Objective 6 Summary

The objective of establishing traceable and reliable laboratory calibration methods for III-V multi-junction solar cells around Europe was completed successfully. Overall key achievements can be summarised as follows:

- *A world-unique facility developed.* This facility can, for the first time ever, calibrate MJSCs, without the need for the expensive hot-air balloon flight currently used to carry the cells to high altitude for calibration. A set of synthetic calibration methods for MJSCs (using terrestrial means) was also developed, with an uncertainty close to 0.5 %, which is comparable to the measurement uncertainties achievable during the balloon flights. It is noteworthy that a member of the consortium participated at CASOLBA 2017, a balloon flight comparison for the calibration of MJSC component solar cells at high altitudes which took place in April 2017 in Australia.
- *Experiments on MJSC and component cells completed*. After the reduction in calibration uncertainty in component cells, a photocurrent linearity evaluation was performed. The temperature dependence of the open circuit voltage in MJSC was also successfully determined; and a series of experimental studies for the next steps in MJSC calibrations were executed. A goniometric reflectance setup has

been modified for use with component cells and MJSC; and a differential spectral responsivity (DSR) setup has been realised, tested and validated.

- *Synthetic calibration facilities for component cells and whole MJSC established and successfully compared*. Unified calibration procedures and measurement uncertainty budgets were derived from the performed experiments and were included in a good practice guide on multi junction reference solar cell calibration methods. This guide has been distributed to partners and stakeholders. Angular, temperature and spectrally dependant characterisation studies were also completed on MJSC devices and the suitability of an LED based Solar Simulator for quadruple-junction MJSC calibrations was proven.

4 Actual and potential impact

4.1 Dissemination activities and engagement with stakeholders

Scientific publications and presentations

A stakeholder committee, formed of industrial partners (e.g. Alstom, Surrey Satellite, Thales and Bruker) from the photovoltaic and semiconductor industries, closely followed the project as it developed. They endorsed the importance of the results of the project and, within the next five years, plan to use the standards calibrated by partners of this project with the synthetic methods (using terrestrial means) developed in the project.

14 high quality scientific articles have been published in peer reviewed journals such as IEEE Journal of Photovoltaics, Applied Physics Letters and Measurement Science Technology, (see section 6) and 3 articles were published in magazines (e.g. PTB news and METinfo).

The project outputs have been presented in numerous and diversified high profile international conferences leading to more than 40 conference contributions (19 presentations, 22 posters). Some examples of conferences are given below:

- Conference on Precision Electromagnetic Measurements in Rio and Ottawa (CPEM 2014, 2016);
- 10th European Space Power Conference in Noordwijkerhout (ESPC, 2014);
- International and European Thermoelectric Society in Dresden (IETC 2015);
- European PV Solar Energy Conferences in Hamburg and Munich (EPVSEC 2015, 2016);
- 19th International Conference on Molecular Beam Epitaxy in Montpellier (MBE 2016);
- Physics of X-Ray and Neutron Multilayer Structures workshop in Twente (2016);
- Spring meetings of the European Materials Research Society (E-MRS) in Lille (2016) and Strasbourg (2017);
- 13th International Conference on New Developments & Applications in Optical Radiometry in Tokyo (NEWRAD2017).

In addition, master and doctoral theses resulted from the activities of this research project:

- Sampo Hyvärinen, 2015, The irradiance uniformity of the solar simulator for III-V solar cells, Master thesis, Aalto University - School of Electrical Engineering;
- Tom Schulze-Bubert, 2016, Development and preliminary characterisation of a LED-based solar simulator, Master thesis;
- Hans Baumgartner, 2017, Metrology for III-V optosemiconductors, PhD thesis, Aalto University;
- Kévin Louarn, PhD thesis defense planned in February 2018 on the fabrication of tunnel junctions based on III-V heterostructures for high-efficiency MJSCs, Paul Henri Sabatier University.

Training activities (workshops and tutorials)

Training events delivered during the project included:

- two training courses for the consortium: one training course in UK (on S-parameter high frequency measurements) and one-to-one training in France (SMM based measurements);

- five training courses or workshops for external audiences, dealing with the metrology for energy harvesting (UK, 2015), Spectroradiometer and broadband intercomparison campaign (Spain, 2015), MJSC calibration methods at EURAMET TC Photometry and Radiometry expert meeting (Poland, 2016), and Highlights from European Metrology projects (France, 2017);
- e-module training on nanoscale characterisation: “New SMM Applications for Semiconductors & Buried Structures, 2D Materials, and Living Cells in Buffer Solution”. This e-module training is online on the project website.

As a highlight in the final stages of the project a 4-day symposium on ‘Analytical Techniques for Precise Characterisation of Nanomaterials’ (ALTECH) was organised. This symposium was one of the 26 symposia organised in parallel at the European Materials Research Society (EMRS) 2017 Spring Meeting (http://www.european-mrs.com/meetings/2017-spring-meeting). Such a conference currently attracts over 3000 scientists and engineers from industry and academia every year. The impact of the activity was maximised by including presentations on the project results and tutorials in the symposium.

In addition, the consortium has written a good practice guide on multi junction reference solar cell calibration methods. This guide has been distributed to partners and stakeholders.

Impact on standardisation

Members of the consortium are actively involved with national and international standards bodies (*e.g.* IEC TC-82: Solar photovoltaic energy systems and AFNOR UF82). Within IEC TC-82, the project has participated in the process for the creation of standard IEC 60904-1- (Photovoltaic devices - Part 1: Measurement of photovoltaic current-voltage characteristics). The project also attended the IEC Loughborough meeting of TC-82:WG (April 2015) where the creation of standards IEC 60904-1-1 and IEC 60904-8-1 (Photovoltaic devices – Part 8-1: Measurement of spectral responsivity of multi-junction photovoltaic (PV) devices) was further discussed. Thanks to the works performed in the project, the same member has participated in the recommendations regarding changes in the standard draft for IEC 60904-8-1 and has contributed to the implementation of these changes. A pre-standard report defining the characterisation and calibration methods of commercial MJSC devices and supporting the standardisation process of ISO/IEC 60904:8-1 was addressed to IEC TC-82. Furthermore, a report on eSPM based measurements carried out in the project has also been sent to the secretary of IEC TC-113 (Nanotechnology for electrotechnical products and systems) as inputs to standardisation in nanometrology. The ISO TC 229 has then access to this submitted report due to its liaison with IEC TC 113.

Engagement with stakeholders

The project was closely involved with all the European key players in the field of MJSC. These companies formed the stakeholder committee and were closely following the project through interaction with their respective NMI’s or by assisting at various progress meeting. This stakeholder committee consisted of 8 members, including 7 industrial partners who are strongly engaged in the photovoltaic and semiconductor industries.

Some of the stakeholders clearly manifested their strong interest through a constant interaction with the consortium (IQE) and notably by their attendance at the first annual meeting (III-V labs, THALES and AZUR SPACE).

At the early stage of the project, the master thesis of Sampo Hyvärinen (see above) about the irradiance uniformity of the solar simulator for III-V solar cells was made in cooperation between VTT and project the stakeholder Endear Oy.

III-V labs actively contributed in the project by distributing single tunnel junctions among the consortium.

Throughout the project, Keysight Austria was heavily interested in the work and used the knowledge on III-V characterisation to promote their SMM. Back to back presentations at scientific conferences led to increased visibility to the different communities for Keysight, METAS and LNE.

4.2 Effective cooperation between JRP-Partners

The work within the project represented a very well balanced mixture of different scientific fields from physics and growth techniques of III-V materials to the modelisation of photovoltaic mechanisms, through the metrological characterisation of devices and the calibration of the solar cells.

The excellence of the work in this project benefited from the high level of collaboration within the consortium throughout the program. For example, the fruitful exchanges through on-site visits, webmeetings or conference calls between:

- Keysight Austria, LNE, METAS, and NPL for eSPM based measurements.
- CEA, CNRS, Keysight Austria, LNE, and METAS on the calibration of SMM for dopant profiling measurements using n doped staircase structures on GaAs;
- CEA, Imperial College and NPL for sample preparation;
- CEA, CNRS and LNE on dopants concentration and free carriers measurements, such measurements being of high interest for modelling tunnel junction devices (modelisation jointly performed by CNRS and LNE);
- CEA and FhG for investigation of the AlGaInP and InGaP heterostructures by means of low temperature photoluminescence;
- CEA and PTB on the GIXRF experiments and the SIMS quantification
- AZUR SPACE, INTA SPASOLAB and PTB for the development and calibration of component and Multi Junction solar cell standards;
- PTB and TUBITAK through an extensive dialog to establish component and multi junction solar cell calibrations in Turkey.

This strong collaboration is exemplified by the dispatching of samples (managed by different partners) among the other involved partners and consequently stimulating exchange of information and experimental data on those samples.

4.3 Examples of early impact

Calibration of multi-junction solar cells

In the field of MJSC calibration at least one funded partner, one unfunded partner and one stakeholder directly profit from the early results of the project. For PTB the precision of its component cell calibration service in an important field like space photovoltaic is crucial for keeping current and the acquisition of new customers. Also additional revenue was already generated by calibration services in this field at PTB within 2015. For possible upcoming calibrations of tandem solar cells from novel materials (organic, perovskite, thin film, hybrid, etc.) the establishment of SI-traced MJSC calibration methods during this project was also necessary.
Due to the large interval between the established balloon flight calibrations of several years the availability of laboratory based calibration facilities is also important. The manufacturer AZUR SPACE (unfunded partner of the project) plans to utilise standards which are calibrated with the synthetic methods (using terrestrial means) developed in this project within their metrology department. The stakeholder AIRBUS D&S "*welcomes the recent results of the EMRP SolCell project. The achieved reduction in measurement uncertainty of component solar cells can directly improve the metrology at AIRBUS D&S".* ESA has also demonstrated their interest on the outputs of the project through the statement below:

- *ESA Document - Comparison of primary (balloon flight) and synthetic calibration of solar cells – p18. June 2015: "Considering that the PTB aims for arriving at an uncertainty in their calibration procedure of 0.5% (without considering an uncertainty in the reference spectrum) one can expect an overall uncertainty of synthetic methods of around 0.6% [...] which is then even slightly lower compared to the uncertainty quoted for the balloon calibration by CNES."*

This last statement should be verified very soon since PTB has just participated at CASOLBA 2017, a balloon flight comparison for the calibration of MJSC component solar cells at high altitudes which took place in April 2017 in Australia. It is then expected that the competitiveness of the developed calibration method will be proven so that more companies and institutions will trace their MJSC metrology to laboratory based calibrations.

Furthermore, at the early stage of the project, two other early impacts must be pointed out:

- the high gain transimpedance amplifier developed in this project by VTT is now commercially available from the company Hasseb;
- INTA has helped one end user, the Finnish solar simulator manufacturer Endeas Oy, to solve issues in uniformity measurements by bringing their expertise on calibration of component cells and triple junction MJSC using single and multi-source solar simulators.

Standardisation

The PTB report on the results of the Laser-based differential spectral responsivity measurement campaign and the experiences gained by the application of ISO/IEC 60904:8-1 draft (Measurement of spectral responsivity of multi-junction PV devices) has supported the coordinator and the IEC- TC82 in finalising and adopting the draft. The standard IEC 60904-8-1 was published on May 2017.

Nanoscale dopant density measurement using SMM

Keysight Austria, LNE and METAS have taken advantage of using the n doped staircase structure on GaAs fabricated by LAAS to successfully calibrate SMM for dopant profiling measurements thanks to a METAS algorithm which models the influence of dopant density as difference in the tip sample capacity. The doping level of this reference structure was determined after MBE growth by SIMS techniques at CEA.

This result is a first demonstration of the enhancement of the SMM capabilities from Si based structures to III-V semiconductors and marks a significant step to the development at LNE and METAS of the traceable metrology at nanoscale for III-V material characterisation.

4.4 Potential impact

Scientific and metrological impact

The project has contributed to a better understanding of key III-V semiconductor transport properties in complex heterostructures with particular respect to nanostructured material. The close collaboration within the consortium will continue, in particular on the metrology for eSPM and calibration activities related to MJSCs. Moreover, the technical reports and data resulting from the project are available to industry and academia across Europe, and will feed into standards bodies for even wider dissemination.

The project provides a clear exploitation path towards further increase of III-V MJSC efficiency, while lowering manufacturing costs and time to market for III-V MJSC based systems and work to improve device efficiency for the terrestrial and space market. Focusing on industrial needs and having partners who closely collaborate with PV cell and systems manufacturers will undoubtedly ensure an effective transfer of the results of this project into industry, reinforced by work on standardisation of material characterisation and material database. In particular:

- The traceable metrology at the macro and nanoscale for material characterisation developed in the project enables the design of current III-V triple-junction solar cells to be optimised in terms of combination of energy band-gaps of the sub-cells, the photocurrent within each cell and the optimised tunnel-junction between cells. The data generated will be directly used by European industry to design new materials stacks and to increase the current efficiency from ~44 % to 50 %; a value that is considered as a tipping point for wider commercial acceptance by industry experts;
- The calibration methods and standards developed reduce the uncertainty in the calibration of triple junction solar cells to the level of that for existing silicon solar cells (0.5%) and also extend these capabilities to enable measurements to be performed on MJSCs with more than three junctions (i.e. four junctions);
- A Good Practice Guide on calibration procedures for MJSC has been produced for the national metrology institutes. This includes the unified calibration procedures drawn up on primary component cell DSR calibration, solar simulator calibration and relative DSR measurements;

- A GaAs staircase dopant density sample has been developed as a new reference structure for the users of SMM in NMIs and in R&D laboratories from academia or industry involved in semiconductor sector;
- New III-V calibration samples were realised for SIMS techniques. More than ten different III-V calibration samples have been realised and added to the SIMS library of the partners. This will help future quantifications of dopant concentration in III-V materials.

Longer term and indirect impact

The research developed in the project has a direct important impact on various European PV stakeholders (equipment, PV cell and module integrators and manufacturers, III-V material suppliers, test and certification institutions, and end-users). Consequently, this will help to strengthen the capability of Europe to maintain and develop a profitable and sustainable solar cell manufacturing base, which is of key strategic relevance both in economic and political terms contributing to meet the EU's objective of 20 % renewable energy and 20 % target on energy efficiency.

The materials metrology improved in the project for III-V materials combination is expected to impact on a variety of other sectors, which are not always directly related to energy production, but are always a key component in our energy consumption (improved device efficiency and reduced thermal loss will have a major impact on our energy consumption). Moreover III-V technologies have been key to many major lifestyle-influencing technologies, *e.g.* displays and lightning (light emitting diodes), internet (diode lasers), optical data storage (lasers for DVD, Blu-ray) and mobile phones (power amplifier).

A tried and tested route for improving device performance involves the introduction of new, superior material combinations. The materials metrology developed in the project will allow the design of new systems to be based on accurate modelling and reduce the cost of development. The integration of III-V technology with existing CMOS materials could also lead to a range of breakthrough systems in digital electronic and in optoelectronics.

Financial impact

The global solar PV market will be worth US$134 billion by 2021. International systems integrators and systems providers are international groups with activities across the world. However, a significant part of the added value lies in the materials, component and subsystem supply chain. Europe has a series of companies acting either as system providers (AZUR SPACE) or are world-class at the component and wafer supply stage: IQE provide epiwafers for III-V devices; CST provides volume III-V processing capability based on a foundry business model; AIXTRON and RIBER provide equipment for growth of III-V based epiwafers for all sectors; OMMIC provides III-V wafers for microwave products; InPACT provides InP wafer for solar cells.

Environmental impact

The world's cumulative PV capacity surpassed the impressive 100-gigawatt (GW) installed electrical power mark, achieving just over 102 GW. This capacity is capable of producing as much annual electrical energy as 16 coal power plants or nuclear reactors of 1 GW each. Each year these PV installations save more than 53 million tons of CO_2. In this way meeting government targets of an 80 % reduction of 1990 CO_2 emissions by 2050 are possible.

In contrast with other PV technologies, III-V MJSCs require much less aperture area due to the high concentration of solar energy contributing to saving large arable lands to be dedicated to agriculture purposes.

The outputs from the project contribute to ensuring the commercial viability and underpinning production of energy efficient semiconductor devices. By developing energy-efficient products, the generation of CO_2 can also be reduced.

5 Website address and contact details

The address of the project public website is http://projects.npl.co.uk/solcell/.

Contacts

Questions about the project: François Piquemal, LNE, francois.piquemal@lne.fr

Questions on metrology for solar cells: Florian Witt, PTB, florian.witt@ptb.de

REG Researchers:

- Diego Alonso Alvarez, Imperial College, d.alonso-alvarez@imperial.ac.uk
- Guilhem Almuneau, LAAS, guilhem.almuneau@laas.fr
- Christophe Licitra, CEA, christophe.licitra@cea.fr

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