European Union
FP7
AMON-RA (214814)

FINAL REPORT TO EUROPEAN COMMISSION

Abstract

We report on the activities carried out and the results obtained within the FP7 project AMON-RA, Architectures, Materials and One-dimensional Nanowires for Photovoltaics – Research and Applications, contract no. 214814. The main goal of the project was to demonstrate a dual-junction photovoltaic cell on silicon substrate based on a nanowire architecture in a cooperative effort of six partners. In AMON-RA, we combined the excellence in materials science at Lund University (ULUND) and the world-leading experience in photovoltaics at the Fraunhofer Institute for Solar Energy Systems (ISE) with the capabilities in processing of nanowire materials and the ambitions in fabricating nanowire-based photovoltaic components at the company Sol Voltaics AB (SOL). All this was supported by state of the art materials and device characterization and structure modeling. Novel ground-breaking photovoltaic materials was developed by ULUND by the use of nanowires that were supplied to the Technical University of Denmark (DTU) and the Johannes Kepler University Linz (JKU) for detailed structural characterization, SOL processed the PV structures, which were measured by ISE, supported by modeling from ISE and University of Kassel (UKAS). The ultimate ambition of the partners was to evaluate the potential of a proposed and dramatically different solar cell architecture which promises to exceed the current price/performance limitations of commercially available cells and to obtain a thorough understanding of fundamental and device-relevant physical properties of nanowires applied to photovoltaic applications.

The project was based on a collaboration between theoreticians that simulated and experimentalists that fabricated and characterized the structures. This project was carried out in a true European spirit with an increasing interaction between the different partners over the course of the project.

We can report here that:

- the project was running at high speed,
- most project goals have been achieved,
- some results have been exceeding the envisioned goals,
- however, not all anticipated milestones could be reached.

The project has led to the first steps of the development of a new type of solar cell structure based on semiconductor nanowires that have the potential to exceed all reported solar cell efficiencies. However, with the end of the project no financial support is at hand to continue this development which certainly would increase the competitiveness of Europe in this very important industrial and energy sector.

Short history of the project

The project AMON-RA was an implication of a call in the FP7 Cooperation Work Programme Theme 4 "Nanosciences, Nanotechnologies, Materials and New Production Technologies – NMP" published 22 December 2006. For the first stage evaluation, a proposal was submitted on 4 May 2007 fitting the topic NMP-2007-2.2-3 "Advanced material architectures for energy conversion" within the activity area "Knowledge-based

smart materials with tailored properties". The first-stage proposal included four partners from three countries, Lund Univ. (Sweden), Fraunhofer ISE (Germany), Atomistix A/S (Denmark) and QuNano AB (Sweden), with a requested funding from EC of 3.325 Mio€. This first-stage proposal resulted in an invitation to submit a full proposal.
While preparing the full proposal, we realized that the expertise of Atomistix would not fit the goals of the project. As a consequence, Atomistix as a partner was replaced by ETH Zürich, Johannes Kepler University and Technical University of Denmark providing experience necessary for the realization of the project. The full proposal was submitted to Brussels on 13 September 2007 and included a requested funding from EC of 3.917 Mio€.
The evaluation of this proposal was very successful with marks 4.5 out of 5 for all three criteria (scientific and technological excellence, quality of the management and potential impact). The project AMON-RA became the only granted PV project out of 30 full proposals in this area, however, with a request of a lowered budget to a maximum of 3.2 Mio€. It should be noted, however, that the reviewers of the proposal had not fully understood the project since they were at one place referring to " synthetic strategies for metal nanowires" which would not comply with the strategies of using semiconductor nanowires.
The negotiations to actually start the project were rather lengthy due to two reasons. On one hand the European Commission had problems implementing the new system for FP7, and on the other hand QuNano AB decided to split the different activities and spun-out the daughter company Sol Voltaics AB for the PV activities. Finally, the AMON-RA project started on 1 October 2008, however, it was not before 18 November 2008 that the contract was signed by the EC. The total budget was adjusted to 4.174 Mio€ with an EC contribution of 3.199 Mio€.
About the time of the project start, Bernd Witzigmann, the site leader at ETH Zürich decided to accept the offer of a chair position at the University of Kassel. Since the contributions of this group were of utmost importance for the outcome of the entire project, the consortium requested an amendment of the contract to exchange partner ETHZ by UKAS. This request arrived at Brussels when the Project Officer for AMON-RA, Patrice Millet, was to leave for a different position. A new PO was assigned in January 2009, Erno Vandeweert. After clarifying the procedure and re-submission, the amendment was approved on 28 April 2009. The project had thus officially seven partners, ULUND, ISE, ETHZ, SOL, JKU, DTU and UKAS. ETHZ left the project on 19 November 2008 and UKAS entered the project the very same day. ETHZ never used nor received any finances from the project. Thus, in reality the consortium was composed out of six partners.

Managing the project

Managing the project had five main tasks:
- to form a team of project partners
- to increase the interaction between the project partners
- to lay the scientific and technological ground to achieve the final goal of the project
- to continue the successful scientific and technological work
- to complete all sub-projects and to finish the project.

It can be concluded that all tasks were achieved. The partners formed within a short time a functioning group with plenty of interactions and certainly working towards the common goal. Already with the kick-off meeting, the partners developed team spirit. This was developed even further in all meetings afterwards.
The consortium had two general meetings per year. All meetings followed a schedule with a joint dinner on the evening of day one and detailed discussions on day two. The attendance to all meetings was excellent with a total of more than 20 representatives from all six partner groups within the consortium at every meeting. At the meetings, all groups presented their latest achievements and results and we always had very intense and open

discussions on the next steps and tasks. These meetings alternated between the different home places for the six partners.
The M36-meeting in October 2011 had a special character since it was co-organized with the Nordic Top-level Research Initiative NANORDSUN (www.nordicinnovation.org/projects/semiconductor-nanowire-based-solar-cells-nanordsun). Via this co-organization, we had the possibility to interact with other researchers interested in nanowire PV structures.
Besides the fruitful and intense meetings the partners had many person-to-person communications on sample design, sample exchange, task details, results, manuscripts and reports. This communication was mainly carried out via email, telephone and partly via the internal website of the project (www.amonra.eu). Also short visits of a researcher from one partner at the side of another partner had been arranged. Further, the coordinator had telephone and email contacts with the site leaders.
Additionally, the coordinator had several email and telephone contacts with the PO.

Progress in the project

The project was organized in seven work packages, with the seventh being management. The work packages had been carefully chosen in terms of congruent competence areas. Each work package involved activities of more than one partner and the leading partner was chosen from the most experienced one in that area. It was planned and executed that all work packages run over the entire period of the project, except WP5, which dealt with characterization of fabricated solar cell structures and thus started upon availability of the first device that had been fabricated (M12). From that point on all work packages were running in parallel until the end of the project.
The main idea behind AMON-RA was to make arrays of light-harvesting nanowires on silicon substrates. The structure intended was composed of nanowires including tandem photovoltaic cells, based on heteroepitaxy of III–V semiconductors. We intended to investigate two different architectures: The first, called "Light Guiding”, consisting of core-shell nanowires with a diameter equal to or greater than λ/n, in which the sunlight shall be guided through materials with decreasing band gap. The second architecture, called "Effective Medium”, consisting of denser arrays of thinner wires, where the light waves will experience an effectively averaged medium as they propagate downwards. The connected Milestone MS7 that was intended to make a decision on the final path of the project was already reported with MS4 when we agreed to proceed to research with the most promising architecture, effective medium, to determine its potential and limitations.

WP1 had the objective to control the growth of the nanowires. The effects of growth parameters on composition, doping and structure were addressed. Four partners were involved with ULUND and SOL having the main task to grow wires while DTU and JKU were mainly involved in characterization of the grown wires, which served as necessary feedback to the growers. ULUND was the lead partner.
The main goals of WP1 were:
• Develop the incorporation of dopants during nanowire epitaxial growth
• Optimize catalyst-assisted and non catalyst-assisted growth on III–V substrates
• Achieve epitaxial growth of III–V nanowires on Si
• Control and optimize III–V nanowire heterostructure segment growth and composition in nanowires, both axially and radially
• Optimize core shell growth for nanowire surface passivation and light guiding
• Evaluate the growth feasibility of III–V nanowire materials in materials combinations predicted for optimal solar cells

• Development of Esaki tunnel diode for incorporation into dual junction nanowire solar cells.
Much work had been done in this WP and results were reported in a number of Deliverables (D1.1, 1.2, 1.3, 1.4 and 1.5) and had been important for all Milestones except MS4 and MS9. The growth activities have been continuously developed with a tremendous improvement. While we started with aerosol nanoparticles we have developed all parts necessary to reach the final goal of a dual-junction nanowire solar cell structure. Work to grow from imprint-defined seed particles started in the last period of the project. Those results will enable us to grow the structures that, according to the simulations made within the project, will lead to higher efficiencies in a future continuation of the project.
The new samples really boosted the efficiency of our structures. Still, the structures used during the final period of the project were not perfect. The picture illustrates the difference in nanowire density and uniformity when changing from aerosol seed particles to imprint seeds.

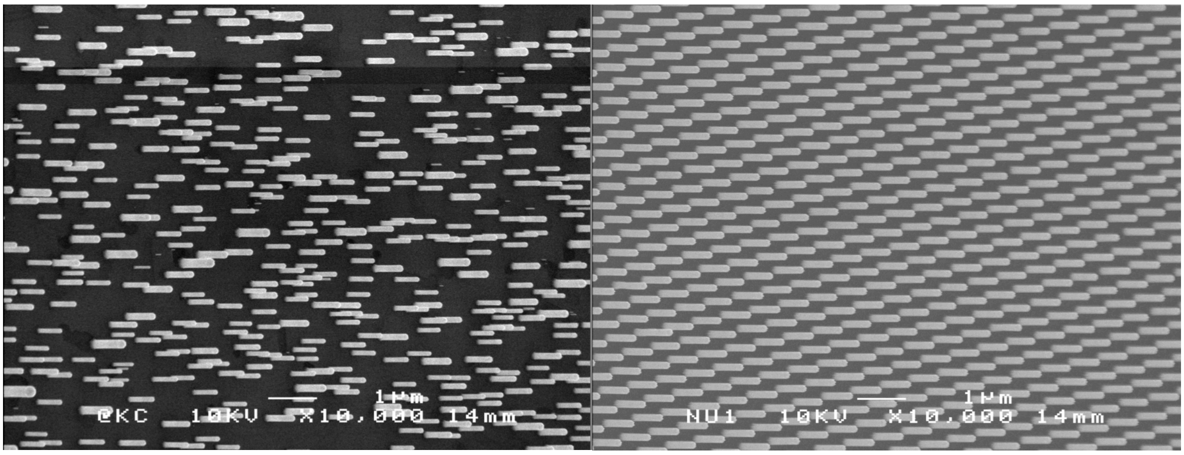


Figure 1: Comparison of nanowires grown from aerosol particles (left) and imprint-defined seeds (right).

The new samples really boosted the efficiency of our structures. Still, the structures used during the final period of the project were not perfect.
It should be mentioned here that the transition from the aerosol particles to the imprinted seeds had been rather complicated. We have been working extensively on imprinted substrates and had to overcome a number of obstacles that prohibited good, reliable, uniformly and repeatedly structures. Not only the preparation of the substrate was a problem but also the larger diameter and the higher density of the seeds changed the growth and we needed to adjust growth parameters. We thus worked on two lanes: (a) aerosol-seeded growth for the further development of post-growth processing and measurement techniques and (b) development of the imprint-seeded growth.
We have studied catalyst-assisted and non catalyst-assisted growth of nanowires. While the catalyst-assisted growth has reached a high degree of understanding, the non catalyst-assisted growth was not as successful and thus terminated.
We have realized controlled doping of the nanowires, both p-and n-type, especially in InP nanowires.
We have reached a high degree of epitaxial growth of III-V nanowires on silicon substrates. Here, we succeeded for the growth of Ga-based nanowires, i.e. $GaAs_xP_y$, a nucleation yield very close to 100%. For In-based wires, i.e. $InAs_xP_{1-x}$, a yield close to 50% was achieved. However, we did not achieved to grow dual-junction nanowire structures on silicon.
We developed an in-situ etching process that allows the complete control over axial and radial growth. This process was developed for In-based wires but is rather generic and was applicable for other materials as well.

Several types of heterostructures have been produced. Nanowires with a GaAs nucleation, followed by GaAsP sections with varying As and P contents can be produced by adjusting the ratio between AsH_3 and PH_3 in the reactor atmosphere. The same approach was used to make InAsP wires with an InP nucleation. Switching of the group-III material has been demonstrated by growing a GaP section on InP nanowires nucleated from a Si substrate, as well as an InP section on InGaP wires grown on a Si substrate with an epitaxial GaP coating. Shell growth for Ga-based nanowires has been demonstrated by an increase of the temperature after growth of the nanowires to deposit a layer of GaP. This resulted in an epitaxial layer of GaP shell surrounding the wire.
We have demonstrated single nanowire Esaki tunnel diodes with high performance. Our non-optimized devices display peak current densities of up to 329 A/cm^2, and we intend to exploit this design for nanowire-based multi-junction solar cells in the InAsP-GaAsP materials system.
We can also report the growth of radial GaInP with varied materials composition on InP as needed for one way of passivating the active wire. Here, we also found a clear obstacle for the further development of the architecture with a light guiding shell due to requirements on lattice matching found. Together with the modeling this enabled us to decide rather early on pursuing only the development of one architecture within the project.
Also, the growth of dual junction PV structures in the GaInP materials system has reached a high degree of maturity.
The developments in the growth have, together with the developments in post-growth processing and measurement techniques, led to a number of real-world characterization of finalized PV structures, with astonishing device efficiency.

WP2 had the objective to develop the process technology necessary to make functional PV cells from nanowires. This required innovative steps, development of suitable processes, as well as adaptation and application of established processes. WP2 was also responsible for the processing involved in production of PV cells for further testing and evaluation. Three partners were involved in this WP, with SOL being the main and the lead partner, assisted by ISE and DTU. The main goals of WP2 were:
• Create low-resistive transparent contacts to nanowire arrays
• Develop a metallic contact grid for maximum efficiency
• Passivate nanowire surfaces to reduce recombination and resistance.

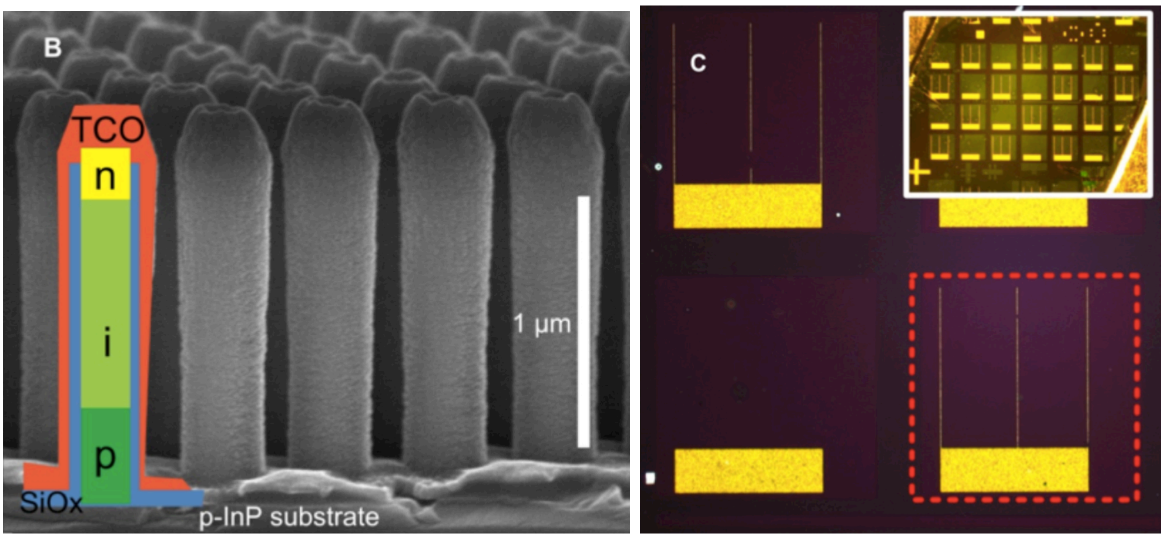


Figure 2: SEM image of processed NWs. The superimposed schematics illustrate the silicon oxide (SiO_x, blue), transparent conducting oxide (TCO, red) and the p-i-n doping layers in the NWs.(**C**) Optical microscope image of NW solar cells. The dashed red line highlights the border of a 1x1 mm^2 cell.

Results from the work in this WP have been reported in four Deliverables D2.1 - 2.4 and have been important for four Milestones MS2, 4, 7 and 10.

As mentioned above, the pre-growth patterning has been an essential part of the development work. We started out with aerosol-defined patterns that served for many of the developments in WP1 but could not be used to optimize the structures. We have developed an imprint method to generate patterns that more resemble the predicted optimized structures and have been more successful with the imprinted patterns during the last period of the project. One example of overgrown imprinted patterns can be seen in Figure 1.

Post-growth patterning has reached such a degree of maturity that we are able to routinely fabricate samples from the grown structures that can go to the device characterization. Still, the processing is not optimal and we foresee a much higher efficiency of the final PV structure in case we would have the possibility to improve processing further. One example of the post-processing can be found in Figure 2.

WP3 had the objective to obtain a thorough understanding of fundamental and device relevant physical properties of nanowires intended for photovoltaic applications. A precise characterization of the grown nanowires is crucial to understand and optimize the growth schemes. It is crucial to develop efficient techniques to measure the energy spectrum, and energy absorption spectrum thereof, and to understand the consequences for the electronic and structural properties. Important device parameters like absorption efficiency and carrier concentration needed to be evaluated for these nanowire structures. Five partners were involved in this WP with JKU being the main and the lead partner, assisted by ULUND, UKAS, ISE and DTU. The main issues were nanowire shape and size, chemical composition, crystal structure and defect characterization, especially for heterostructures and wires with different doping levels.

Results from the work in this WP have been reported in five Deliverables D3.1 - 3.5 and have been important for almost all Milestones except MS8 and 10.

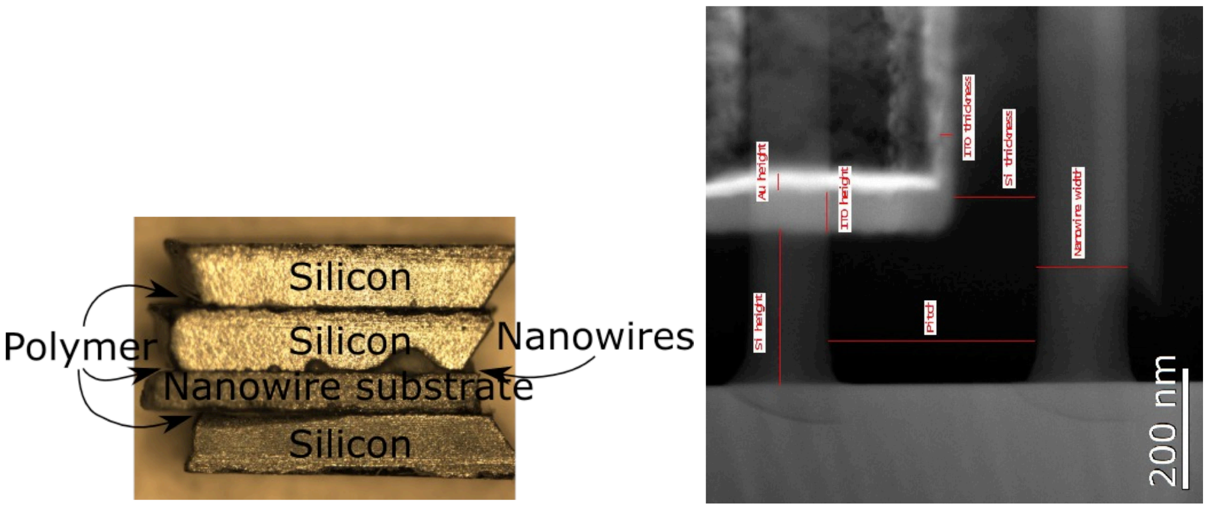


Figure 3: Left: Picture of the preparation set-up to be able to obtain TEM pictures of the processed structures. Right: One actual TEM micrograph of a processed structure.

Many different methods have been applied to characterize the structures, especially different microscopy, x-ray, and luminescence techniques. The measurements gave plenty of insights into the morphological and structural properties and the physics of the wires.

The intense communication between the growers from ULUND and SOL with the physicists from JKU and DTU ensured that the observations had a direct input in the growth experiments. From the morphological and structural observations, the growers could modify the process parameters in order to improve the structures. However, one of our internal dreams we could not achieve: to characterize one single fully processed structure by x-ray, electron microscopy as well as electrically.

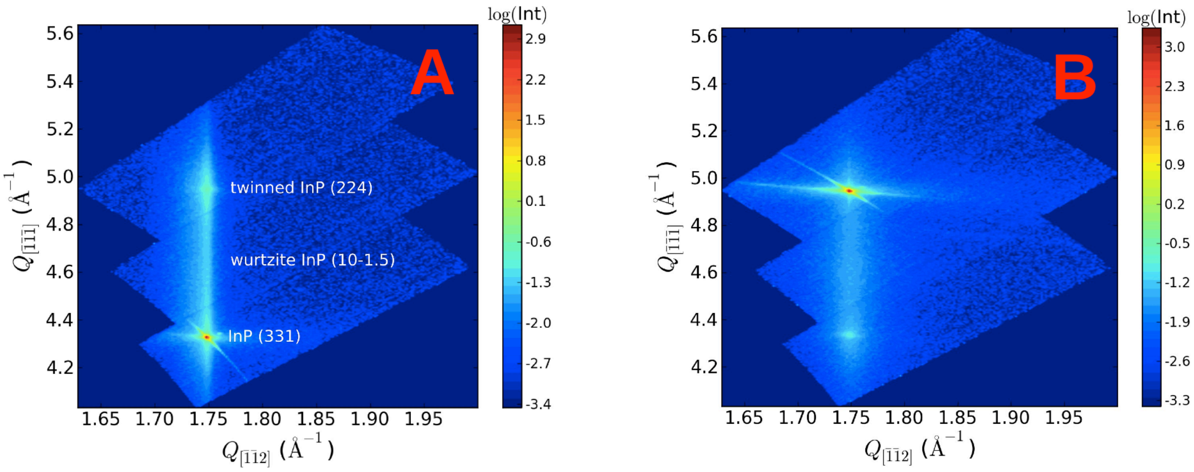
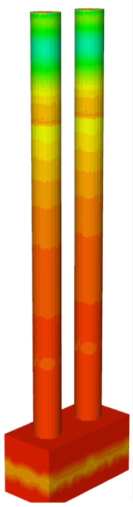


Figure 4: Asymmetric reciprocal space maps from XRD measurements of processed structures with silicon oxide (A) and polymer (B) as isolation.

WP4 had the objective to develop novel models, analyze the physics, and to develop the ultimate performance design for nanowire solar cells. The methods were physics-based and aimed to be predictive, i.e., by knowing the geometry, materials, and microscopic material parameters of the solar cell, the electrical and optical characteristics are calculated as in an experiment. Model verification was ensured by detailed comparison to experimental data determined in WP3 and WP5. The results were used to analyze and interpret experimental results, study the underlying physical mechanisms and develop novel designs at the computer.
Originally, it was planned that two partners (UKAS and ISE) would work in this WP, however, even ULUND joint this task. The reason being on one hand that UKAS had some delays since the group moved from Zürich to Kassel in the first months of the project and on the other hand that ULUND had some extra capacity for such simulations. UKAS was the main and lead partner in this WP.



Geometry

· **Length**: 2000 nm **Diameter:** 160nm / 280nm **Pitch**: 300nm/500nm

Illumination

· **Spectrum:** AM 1.5d
· **Concentration**: 1 x and 500 x
· **Incidence:** normal

Material

· **Material system:** InP/InAs
· **Mole fractions**

Material arrangement

· **Structure**: axial / core-shell
· **Subdivision** of the nanowire into top (core) and bottom (shell) domain
· **Placement** of the pn-junctions within the top (core) E_{g1} and bottom (shell) E_{g2} domains
· **Doping Levels**

Figure 5: Description of simulation parameters.

The main goals of WP4 were:
• Definition of suitable bandgap energies for single-and dual-junction nanowire solar cells
• Definition of suitable device structure including doping levels and barrier layers
• Definition of optimum configuration for wire length, spacing and diameter
• Understanding of optical and electrical loss mechanism in single-and dual-junction nanowire solar cells with/without light guide structure
• Improvement of electro-optical modeling tools for nanowire materials.
Results from the work in this WP were reported in four Deliverables D4.1 – 4.4 and had been important for four Milestones (MS2, 4, 7 and 10).
Extensive simulations have been performed by all three partners with the emphasis to actually split the work between the three partners involved and use the strength of each partner to accomplish a more complete picture. The optical generation function for nanowire solar cells have been analyzed and the electromagnetic mechanisms for light capture in a nanowire array under solar illumination have been clarified.

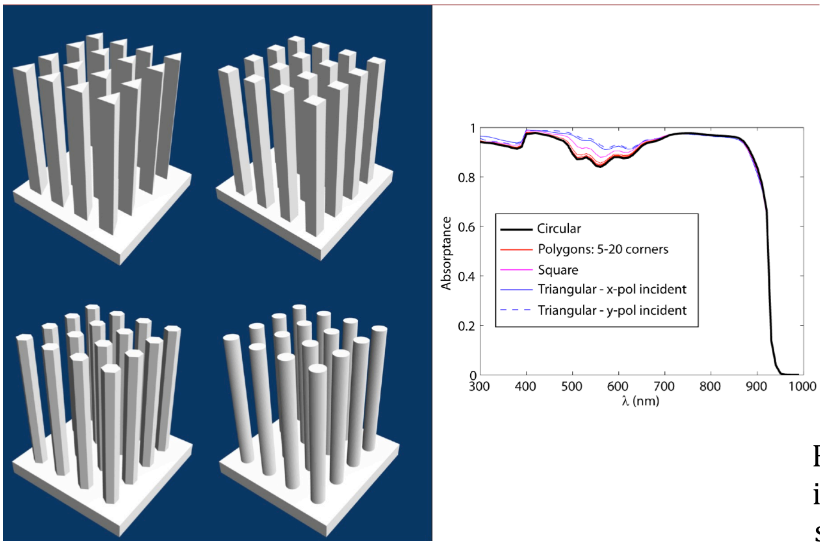


Figure 6: Simulation of the influence of the wire cross shape on the absorptance.

Surely, even in this Workpackage more results could be achieved by a continued support of the project.

WP5 had the objective to characterize nanowire solar cells under standard test conditions in order to determine the efficiency of these devices and to access the behavior and quality of the different layers in the structure. The device characterization was also an important input to WP4 to validate the theoretical device simulation by experimental results. New measurement setups have to be developed to measure multi-junction nanowire solar cells accurately. Two partners worked in this WP with ISE being the main and lead partner, assisted by UKAS. This was especially important since no other nanowire group in the world that works on PV structures has been able to perform such measurements.
The main goals of WP5 were:
• Precise IV and quantum efficiency measurements of single-junction and dual-junction nanowire solar cells with/without light guide structure
• Characterization of nanowire solar cells under concentrated illumination
• Evaluate influence of process technology and characterization on nanowire solar cell performance.
Three Deliverables were within this Workpackage D5.1 – 5.3 and the results were important to six Milestones (MS3 and MS6 – 10). Characterization of fully processed

nanowire PV structures was accomplished with the new measurement set-up developed by ISE during the first reporting period.

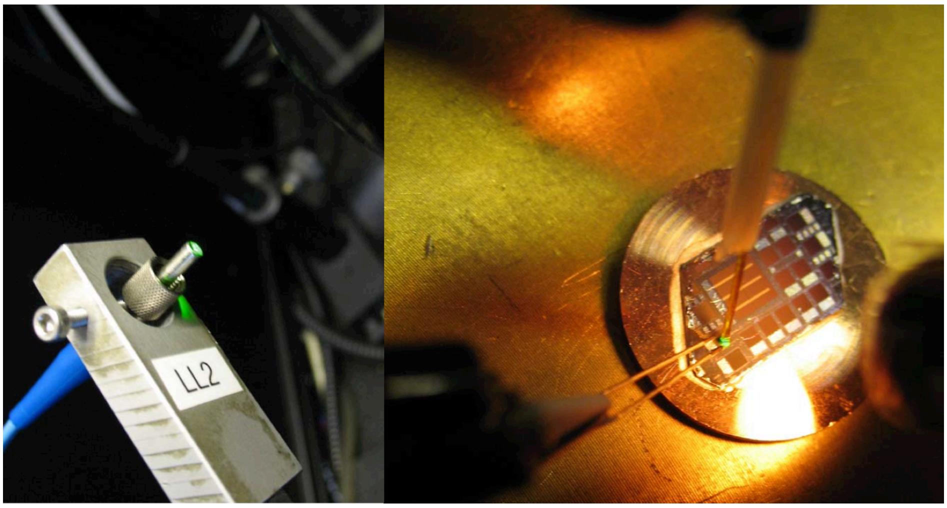
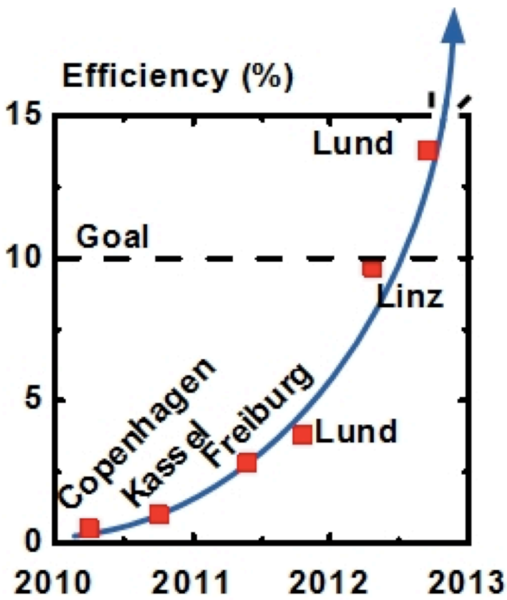


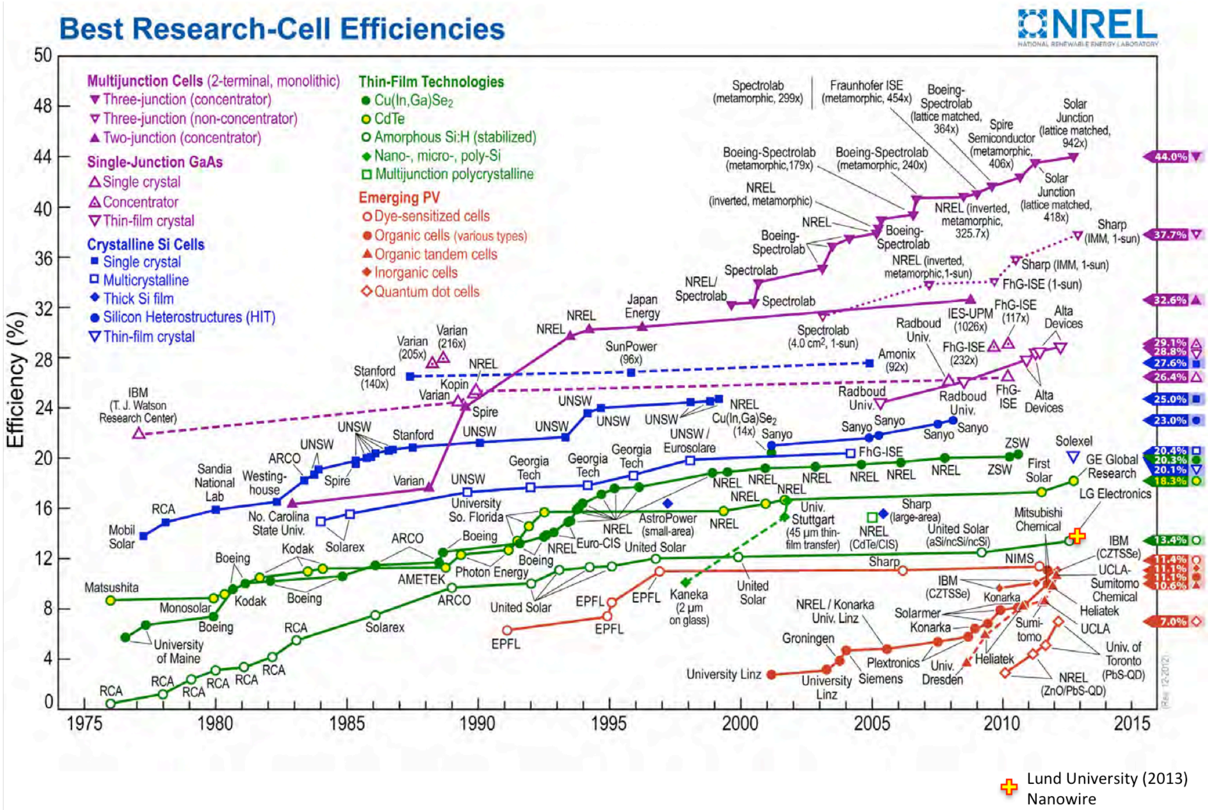
Figure 7: The measurement set-up at ISE.

For the best devices a top efficiency of 13.8 % under 1 sun illumination was determined. This result is better than any so far reported results for so-called emerging PV segment according to the NIST efficiency data.



Efficiencies of the processed PV structures as measured in WP5 during the course of the project, including an optimistic extrapolation.
(The city names refer to the project meeting places.)

WP6 had the objective to communicate the findings of the project to the scientific and technical community, to handle IPR and confidentiality issues, and to produce a roadmap for future development and deployment of nanowire solar cells. Three partners had tasks in this WP with SOL being the main and lead partner, assisted by ULUND and ISE.
Before communicating findings to the public and in order to handle IPR and confidential issues in a correct way, all partners posted their manuscripts on the internal web sites to ensure that all partners could comment and react. The dissemination was mainly done via journal articles and conference contributions, see publications. A roadmap document was developed.



PV cell efficiency data as given by NREL with our result indicated

WP7 was the management WP where ULUND had the main and lead role, assisted by UKAS, SOL and JKU. See above chapter Managing the project.
As illustrated by the Deliverables and Milestones, the project was running accordingly to the anticipated time line. All Deliverables and Milestones have been reported to the EC.

Milestones

All Milestones except MS9 and 10, which contain Deliverable D5.3, have been reported via ECAS.

Deliverables

All Deliverables, except D5.3 have been reported via ECAS.

Use of finances

The use of the finances was reported via ECAS.
At the project meeting in October 2011, we discussed the use of the 100 kEUR for subcontracting as it was anticipated to integrate simulation models into a commercial simulation environment. However, during the course of the project we realized that the partners within the consortium could carry out this task. Thus, we agreed to allocate the planned money of 100 kEUR jointly to the two involved partners, partner 2 ISE and partner 7 UKAS. This was communicated to the PO and approved on 8 November 2011.

Dissemination

The project AMON-RA generated more than 35 publications in international peer-reviewed periodicals which were spread over the scientific community. Results were reported on more than 35 conferences. The conferences attended were chosen carefully to approach the appropriate scientific and industrial colleagues and also by geographical spreading

even outside Europe. By this, we could ensure that the project gets a high visibility in the relevant communities.
As can be seen from the list an increasing number of publications are collaborative publications. It should also be mentioned here, that we were able to widen our cooperation from the consortium to other partners, like Fujitsu and Harvard.
A few more publications will result from the project. Especially, for the report on the main result, the high efficiency of our structures, we submitted a manuscript to Science which is now available online as Science Express: J. Wallentin et al. "InP nanowire array solar cells that achieve 13.8% efficiency through high light absorption". Here, all partners have co-authored except DTU and JKU.
One additional manuscript is under preparation, now including even the characterization results from DTU and JKU, that will summarize the efforts of the entire project and we aim at publication in a PV journal.
Besides publication in journals and on conferences, we had two public lectures given by Frank Dimroth (ISE) and Jerry Olson, the scientific advisor to the project team.

Noteworthy

Jerry Olson, the scientific advisor to the project team received the prestigious Cherry Award from IEEE. The Cherry Award is named in honor of William R. Cherry, a founder of the photovoltaic community. The purpose of the award is to recognize individual engineers or scientists who devoted a part of their professional life to the advancement of the science and technology of photovoltaic energy conversion. It is only awarded to scientists who are still actively contributing to the field (www.nrel.gov/news/press/2011/1451.htm).

Summary

As illustrated by the Deliverables and Milestones, the project was running accordingly to the anticipated time line. All Deliverables and Milestones have been reported to the EC.
We can conclude that the project AMON-RA was running on a high speed generating good and promising results as outcome of a true cooperation between the partners and which was even enhanced during the final course of the project.

Lund, 10 February 2013
Knut Deppert
Coordinator AMON-RA