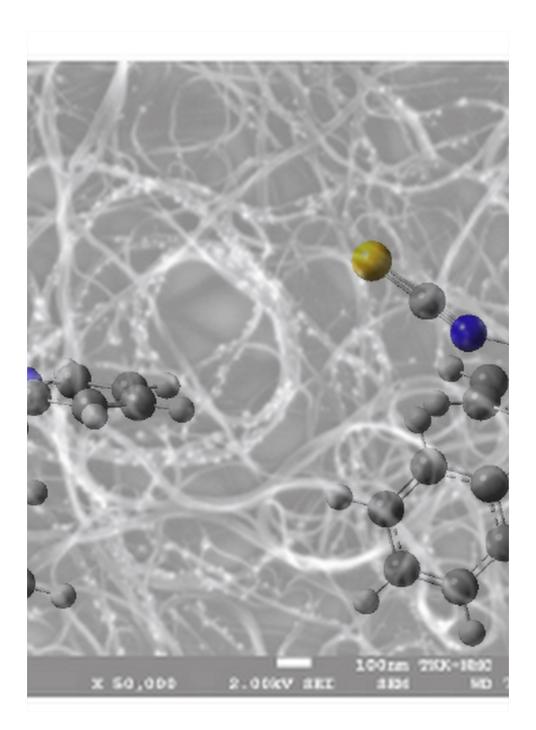


Nordic center of excellence in photovoltaics (NCoE in PV)

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Arve Holt, Marika Edoff, Peter Lund, Hanne Laurizten, Turid Worren, Enn Mellikov, Viatcheslav Andreev



Participants

Norway

Institute for Energy Technology (IFE) Arve Holt Erik Stensrud Marstein Jo Gjessing

Norwegian University of Science and Technology (NTNU)

Turid Worren Ingve Simonsen Tor Nordam

Sweden

Uppsala University (UU) Marika Edoff Charlotte Platzer-Björkman Jonas Petterson

Finland

Aalto University (AU), former Helsinki University of Technology Peter Lund Kerrtu Aitola

Denmark

Danish Technological Institute (DTI) & University of Southern Denmark (SDU) Hanne Lauritzen (DTI) Anders Rand Andersen (DTI & SDU)

Estonia

Tallinn Technological University (TTU) Enn Mellikov Mare Altosaar Kristi Timmo

Russia

Ioffe Physical-Technical Institute of the Russian Academy of Sciences (IOFFE) Vladimir Khvostikov Nikolay A. Kalyuzhnyy

Steering group

Arve Holt, IFE Turid W. Reenaas, NTNU Marika Edoff, UU Peter Lund, AU Hanne Lauritzen, DTI Vladimir Khvostikov, IOFFE Enn Mellikov, TTU

Fact-sheet

Title: Nordic center of excellence in photovoltaics (NCoE in PV)

Authors and organizations

Project manager: Arve Holt Organization: Institute for Energy Technology Address: P.O. Box 40, NO-2027 Kjeller, Norway Phone: +47 63 80 61 95 E-mail: arve.holt@ife.no

Name: Hanne Lauritzen Organization: Technical University of Denmark Address: Building 111, room 8, 4000 Roskilde, Denmark Phone/Mob: +45 46 77 47 28/+45 21 32 53 64 E-mail: hael@dtu.dk

Name: Peter Lund Organization: Aalto University Address: PO Box 14100, FI-00076 AALTO, Finland Phone: +358 40 5150144 E-mail: peter.lund@aalto.fi

Name: Turid Worren Reenaas Organization: Norwegian University of Science and Technology Address: Institutt for fysikk, Realfagbygget, NO-7491 Trondheim, Norway Phone: +47 73590386 E-mail: turid.reenaas@ntnu.no

Name: Marika Edoff Organization: Uppsala University Address: Ångströmlaboratoriet, Box 534, SE 751 21, Uppsala, Sweden Phone/Mob: +46 18 471 72 49/ +46 704-250 895 E-mail: Marika.Edoff@angstrom.uu.se

Name: Vladimir Khvostikov Organization: Ioffe Physico-Technical Institute in St. Petersburg Address: 26 Polytekhnicheskaya str. 194021 St.Petersburg, Russia Phone: +7 812 292 79 24 E-mail: vlkhv@scell.ioffe.rssi.ru

Name: Enn Mellikov Organisation: Tallinn University of Technology Address: Ehitajate tee 5, 19086 Tallinn, Estonia Phone: +372-620 2798 E-mail: ennm@staff.ttu.ee

Key words: Silicon solar cells, CIGS solar cells, dye-sensitized solar cells, tandem solar cells

Abstract: Nordic center of excellence PV is an integrated research project for the Nordic and Baltic region with a focus on solar electricity. In total seven research institutions is involved and the center is coordinated by Institute for Energy Technology (IFE). The aim of the project is to stimulate research and development related to solar electricity in order to strengthen the commercial development of solar cells in the Nordic and Baltic countries. The project covers selected topics within solar cell technology including silicon solar cells, CIGS solar cells, dye-sensitized solar cells and tandem solar cells. The project has successfully educated 7 PhDs with a large portfolio of published papers. The collaboration between the Nordic and Baltic research institutions has been strengthened through several Nordic solar cell conferences. Competence and technology transfer has been achieved through highly specialized workshops for the PhD students as well as exchange of scientific personnel.

Executive summary

Objective

The purpose of Nordic center of excellence in photovoltaics (NCoE in PV) has been to stimulate research and development related to solar electricity in order to strengthen the commercial development of solar cells in the Nordic and Baltic region. Furthermore, the objective has been to tie the institutions closer together and to promote sharing of knowledge between institutions. The topics of research have covered technologies related to crystalline silicon solar cells, CIGS solar cells, dye-sensitized solar cells and tandem solar cells.

Background and approach

The NCoE in PV is continuing the effort from the project Nordic PV (2003-2006) to further strengthen the research activity and network within solar PV in the Nordic countries and to expand it to the Baltic region (Estonia and Russia).

Photovoltaics are now emerging as the most promising source to power the world in the future. This represents an enormous commercial opportunity for technology development for the Nordic and Baltic countries. In order to realize this opportunity, it is important for companies to have access to competence and highly qualified personnel. To secure this, the underlying objectives of NCoE in PV have been as follows:

- 1. Strengthen individual institutions in the participating countries through PhDs, cooperation and knowledge transfer
- Expand the Nordic R&D network to include Russia and Estonia and develop it into a center of excellence effectively serving the fast-growing and demanding Nordic PV industry
- 3. Educate personnel to meet the demand of the Nordic PV industry and to stimulate new commercialization

Integrated research tasks

The NCoE in PV has involved research personnel from all the seven partner institutions (see list of participants) in additions to seven PhD students on full time. All PhD-students have successfully defended their thesis; the last one did so in spring 2013. The research has lead to many international peer-reviewed journal papers and contributions to national and international research conferences.

The research tasks have covered technologies including crystalline silicon solar cells, CIGS solar cells, dyes-sensitized solar cells and tandem solar cells. The results are thoroughly described in the main section.

Network strengthening activities

Conferences, in depth workshops and hands on workshops have been important tools to expand the Nordic network on solar electricity to include Estonia and Russia. Conferences and workshops have been held in Norway, Sweden, Finland and Estonia with invited keynote speakers with good international reputation. At several of these conferences there has been visits to nearby PV companies and social gatherings. These conferences have been extremely important arenas for building of networks.

Exchange of PhD students and scientific personnel is the other main arena for network building and transfer of competence between institutions and technologies. A post doc and a PhD student from Uppsala have spent time at IFE, the Finnish PhD student spent time at Uppsala University and the Danish PhD student visited Aalto University (former Helsinki University of Technology). Admittedly, the exchange was planned to be even more comprehensive, however, difference in fields sometimes made exchange more difficult than expected.

Impact on PV R&D in the Nordic and Baltic region

During this project the solar cell industry has continued to grow at an incredible speed and yearly installations today are more than 10 times higher than at the start of this project. In the same time period the PV landscape has changed completely and most of the manufacturing have moved east towards China. This has of course also had an impact on the Nordic PV industry and the research partners. However, looking at all the companies involved in this project, Elkem Solar (Norway), REC ASA (Norway), Solibro research AB (Sweden), Topsil A/S (Denmark), Energinet.dk (Denmark), Luvata (Finland), everyone of them are still working with PV today. That is quite remarkable considering the number of bankruptcies within the PV industry the last couple of years. We also see now that new companies formed in Norway and Sweden and the number of PV companies in Norway today is twice as high as in 2005¹. This would be very difficult without access to qualified personnel and centers of competence.

Of concrete commercial output of this project is the company EmaZys² started by one of the PhD students in this project, Anders Rand Andersen. His company delivers technological solutions to locate flawed modules in a larger PV system. The technological solution is related to the work performed in his PhD thesis. The company Crystalsol³, formed in 2008, is based on some of the findings of another PhD student in this project, Kristi Timmo.

Perhaps most impressive of all is the fact that all seven PhD students involved in this project have successfully defended their thesis. That implies that the research institutions have contributed with good research projects and supervisors, and that they have been able to attract clever people.

Looking forward

In recent months there have been signs of recovery in the PV industry and the future is looking better than for a long time. On the positive side, the price reductions have lead to cheaper solar electricity and today PV has reached grid parity in more than 100 markets around the world⁴. We see that new companies are emerging in the Nordic countries also in difficult times and there is no doubt that solar energy will be a business for the future. Access to competence will remain vital to seed new tech companies also in the future.

A new trend that has emerged since the start of this project is an increasing installation rate of PV for the Nordic markets. The use of PV has been sparked by market stimulation and rapidly falling PV module costs the last few years. In Denmark the marked for PV have exploded, and Sweden seem to follow. Norway and Finland are some steps behind, but also here the future is likely to be sunny. This part of the value chain has not been a part of this project, but research can play a useful role to develop good solutions suitable for the Nordic environment. A cooperation project on the PV system side could see many synergies and would be a very interesting direction for a future research projects since it equally addresses all participant countries.

¹ <u>http://www.tu.no/kraft/2013/09/27/antall-norske-solenergiselskaper-har-doblet-seg-</u> <u>siden-2005</u>

www.emazys.com

³ <u>http://www.crystalsol.com/engl/news/news.html</u>

⁴ http://reneweconomy.com.au/2013/graph-of-the-day-solar-grid-parity-in-102-countries-39133

Table of Contents

Participants	ii
Steering group	ii
Fact-sheet	iii
Executive summary	iv
Objective	iv
Background and approach	iv
Integrated research tasks	iv
Network strengthening activities	iv
Impact on PV R&D in the Nordic and Baltic region	v
Objective	2
Background and approach	2
Integrated research tasks	2
1. Modelling Band Gap Gradients and Cd-free Buffer Layers in Cu(In,Ga)Se2	
Cells	3
2. Scattering of light from weakly rough surfaces	4
3. Carbon nanomaterials as counter electrodes for dye solar cells	6
4. Photonic crystals for light trapping in solar cells	7
5. Multijunction solar cells with subcells based on germanium	9
6. Formation of Properties of CuInSe and Cu ZnSn(S,Se) Monograin Powders	
Synthesized in Molten KI 7. Life Time attacking for Days consisting d News structure of Salar Calle	9
7. Life-Time studies for Dye-sensitized Nanostructured Solar Cells	11
Network strengthening activities	12
2nd Nordic Workshop on Crystalline Silicon Solar Cells	13
Nordic seminar on modelling of CIGS devices	14
Program Nordic Hands-On Workshop on Crystalline Silicon Solar Cells	15
3rd Nordic PV Conference	15
Nordic Photovoltaic workshop on Stability and Encapsulation	17
Mobility of scientific personnel	17
Impact on PV R&D in the Nordic and Baltic region	18

Objective

Solar energy is mainly accepted to be one of the most important energy sources for the future. The purpose of NCoE in PV has been to strengthen research and development related to solar electricity in order to stimulate the commercial development of solar electricity in the Nordic and Baltic region. The research at each participating institution has been strengthened through a PhD student founded by this project. Furthermore, the objective has been also to tie the institutions closer together and to promote sharing of knowledge between the institutions. The topic of the PhDs has covered technologies related to crystalline silicon solar cells, CIGS solar cells, dye-sensitized solar cells and tandem solar cells.

Background and approach

The Nordic Center of Excellence in Photovoltaics (NCoE in PV) is continuing the effort from the project Nordic PV (2003-2006) to further strengthen and expand the research activity and network within solar PV in the Nordic and Baltic region. NCoE in PV includes Tallinn Technical University of Estonia and the IOFFE institute of Russia in addition to partners from the Nordic countries. A list of all participants are found on page ii) under participants.

During the last decade the solar cell industry has expanded at an incredible speed and has now become a power source that gives a significant contributions to the electricity production in several small and large European countries. PV is now emerging as the most promising source to power the world in the future. From today until 2030 about 7000 billion dollars is expected in clean tech investments according to City Group in a recent report⁵. That's double the amount of all fossil fuel investments put together. In order to realize this enormous commercial opportunity, it is important for companies to have access to competence and highly qualified personnel. To secure this, the underlying objectives of NCoE in PV have been as follows:

- 1. Strengthen individual institutions in the participating countries through PhDs, cooperation and knowledge transfer
- Expand the Nordic R&D network to include Russia and Estonia and develop it into a center of excellence effectively serving the fast-growing and demanding Nordic PV industry
- 3. Educate personnel to meet the demand of Nordic PV industry and to stimulate new commercialization

Integrated research tasks

The NCoE in PV has involved research personnel from all seven participating institutions in addition a full time PhD student at each institution. The research tasks within this project have been focusing on seven areas that are described below. All PhD-students have successfully defended their thesis; the last one did so in spring 2013. The research has lead to many international peer-reviewed journal papers and contributions to national and international research conferences. A list of papers is shown below each thesis.

The research tasks of this project has taken place mainly at University of Uppsala in Sweden, Aalto University (former Helsinki University of Technology) in Finland, Danish Technological Institute and University of Southern Denmark (both in Denmark), Norwegian University of Science and Technology in Norway, Institute for Energy Technology in Norway, Tallinn Technical University in Estonia and the IOFFE institute in Russia. The research has focused on core areas at the different institutions.

⁵ <u>http://reneweconomy.com.au/2013/darwin-69517</u>

1. Modelling Band Gap Gradients and Cd-free Buffer Layers in Cu(In,Ga)Se2 Solar Cells

PhD-thesis by Jonas Petterson, Uppsala University, 2012

Abstract

A deeper understanding of Cu(In,Ga)Se2 (CIGS) solar cells is important for the further improvement of these devices. This thesis is focused on the use of electrical modelling as a tool for pursuing this aim. Finished devices and individual layers are characterized and the acquired data are used as input in the simulations. Band gap gradients are accounted for when modelling the devices. The thesis is divided into two main parts. One part that treats the influence of cadmium free buffer layers, mainly atomic layer deposited (Zn,Mg)O, on devices and another part in which the result of CIGS absorber layer modifications is studied. Recombination analysis indicates that interface recombination is limitting the open circuit voltage (Voc) in cells with ZnO buffer layers. This recombination path becomes less important when magnesium is introduced into the ZnO giving a positive conduction band offset (CBO) towards the CIGS absorber layer. Light induced persistent photoconductivity (PPC) is demonstrated in (Zn,Mg)O thin films. Device modelling shows that the measured PPC, coupled with a high density of acceptors in the buffer-absorber interface region, can explain light induced metastable efficiency improvement in CIGS solar cells with (Zn,Mg)O buffer layers. It is shown that a thin indium rich layer closest to the buffer does not give any significant impact on the performance of devices dominated by recombination in the CIGS layer. In our cells with CdS buffer the diffusion length in the CIGS layer is the main limitting factor. A thinner CIGS layer improves Voc by reducing recombination. However, for thin enough absorber layers Voc deteriorates due to recombination at the back contact. Interface recombination is a problem in thin devices with Zn(O,S) buffer layers. This recombination path is overshadowed in cells of standard thickness by recombination in the CIGS bulk. Thin cells with Zn(O,S) buffer layers have a higher efficiency than CdS cells with the same absorber thickness.

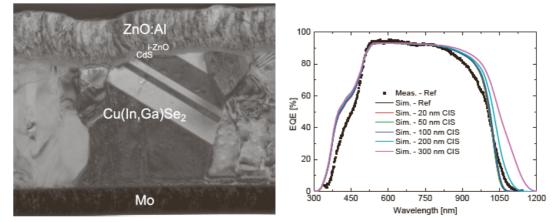


Figure 1: Transmission electron microscope image of a CIGS solar cell (left). Experimental and simulated external quantum efficiency curves for CIS solar cell (right).

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- J. Pettersson, M. Edoff and C. Platzer-Björkman, Electrical modelling of Cu(In,Ga)Se2 cells with ALD-Zn1-xMgxO buffer layers, Journal of Applied Physics 111 (2012) 014509, doi: 10.1063/1.3672813
- J. Pettersson, T. Törndahl, C. Platzer-Björkman, A. Hultqvist, M. Edoff, Influence of absorber thickness on Cu(In,Ga)Se2 solar cells with different buffer layers, Manuscript

2. Scattering of light from weakly rough surfaces

PhD-thesis by Tor Nordam, NTNU, 2013

Abstract

A formalism is introduced for the non-perturbative, purely numerical, solution of the reduced Rayleigh equation for the scattering of light from two-dimensional penetrable rough surfaces. In the papers included in this thesis, we apply this formalism to study the scattering of p- or s-polarised light from two-dimensional dielectric or metallic randomly rough surfaces, or from two-dimensional randomly rough thin dielectric films on metallic substrates, by calculating the full angular distribution of the co- and cross-polarised intensity of the scattered light.

We present calculations of the mean differential reflection coefficient for glass and silver surfaces characterised by (isotropic or anisotropic) Gaussian and cylindrical power spectra, and find a good match with experimental results, as well as results obtained from another numerical method. We also present a numerical calculation of the Mueller matrix for scattering from rough surfaces, based on the same method.

We investigate the optical phenomena of enhanced backscattering, enhanced forward scattering and satellite peaks. Enhanced backscattering is a well known phenomenon, and is used as one among several indicators of correct results. The phenomenon of enhanced forward scattering has not previously been investigated in two-dimensional systems. We demonstrate its presence, and provide an explanation for why it is qualitatively different from the same phenomenon in one dimension. Regarding satellite peaks, there has been a dispute in the literature, where one group found they should be present in scattering from a thin dielectric film on a metallic substrate, while another group found they should not. We have demonstrated their presence, and shown how the one-dimensional phenomenon of satellite peaks become "satellite rings" in the two-dimensional case.

The proposed method is found, within the validity of the Rayleigh hypothesis, to give reliable results. For a non-absorbing metal surface the conservation of energy was explicitly checked, and found to be satisfied to within 0.03%, or better, for the parameters assumed. This testifies to the accuracy of the approach and a satisfactory discretisation. We also perform a numerical investigation of the range of validity of the reduced Rayleigh equation for scattering from two-dimensionally rough silver and perfectly conducting surfaces.

The advantage of using a numerical solution of the reduced Rayleigh equation, rather than a rigorous numerical method such as the surface integral method, lies in the required computational resources. The main limitation of these methods for considering twodimensionally rough surfaces are their memory requirements. To calculate the scattering amplitude for a typical system studied in this thesis, by the reduced Rayleigh equation, requires 12 GB of memory. To solve a similarly sized system with a rigorous method requires one or two orders of magnitude more. The limitation of the reduced Rayleigh equation is that it can only be applied to weakly rough surfaces, due to the assumption of the Rayleigh hypothesis.

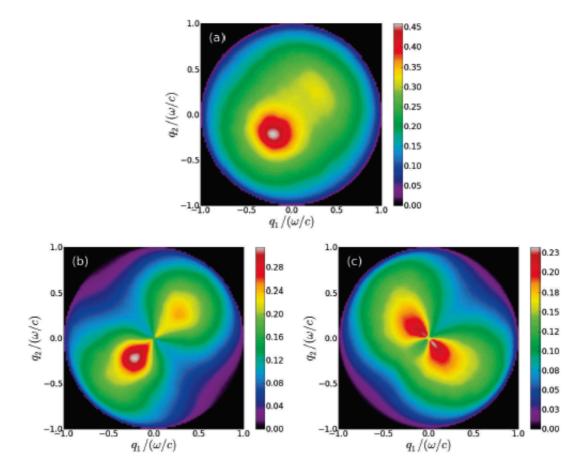


Figure 2: *p*-polarized light scattered off an isotropic perfectly conducting rough surface. The figures show the differential reflection coefficient for *s* and *p*, *s*, and *p* polarization, respectively.

Papers:

- T. A. Leskova, P. A. Letnes, A. A. Maradudin, T. Nordam, and I. Simonsen, "The scattering of light from two-dimensional randomly rough surfaces," Proc. SPIE, vol. 8172, p. 817209, 2011
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- P. A. Letnes, T. Nordam, and I. Simonsen, "Coherent effects in the scattering of light from two-dimensional rough metal surfaces," Submitted to Journal of the Optical Society of America A, 2013

3. Carbon nanomaterials as counter electrodes for dye solar cells

PhD-thesis by Kerrtu Aitola, Aalto University (former Helsinki University of Technology), 2012

Abstract

- 1. The dye solar cell (DSC) is an interesting emerging technology for photovoltaic conversion of solar electromagnetic energy to electrical energy. The DSC is based mainly on cheap starting materials and it can be manufactured by roll-to-roll deposition techniques on flexible substrates, which is considered as one option for cost-effective large-scale solar cell production.
- 2. The most expensive component of the DSC is the transparent conductive oxide glass substrate, and considerable cost reductions can be achieved by changing it to e.g. a plastic substrate. Plastic substrates are very flexible, lightweight and transparent. The state of the art DSC catalyst is thermally deposited or sputtered platinum, but platinum is a rare and expensive metal. Carbon, on the other hand, is widely available and some of its nanomaterials conduct electricity and are catalytic toward the DSC counter electrode (CE) reduction reaction.
- 3. In this work, carbon nanomaterials and their composites were studied as the DSC CE active material. The materials were random network single-walled carbon nanotube (SWCNT) film on glass and plastic substrate, vertically aligned multiwalled carbon nanotube "forest" film on steel and guartz substrate and carbon nanoparticle composite film on indium tin oxide-polyethylene terephthalate (ITO-PET) substrate. After comparison of the materials, the SWCNT network film on PET was chosen as the main CE type of this study, since it offers superior conductivity, transparency and flexibility over the other carbon-based CEs, it is also the thinnest and contains only one active material component. When a 30 % transparent SWCNT network film on PET was tested as a DSC CE, it was found out that such a film is not catalytic and conductive enough for a full 1 sun illumination DSC device, but the film could be suitable for a indoor illumination level application. The catalytic properties of a 10 % transparent SWCNT film were improved by depositing conductive PEDOT polymer on the film, and the DSC with such film as the CE had similar efficiency than the reference DSC with a sputtered Pt on ITO-PET CE. The PEDOT-SWCNT film had superior catalytic performance over the studied Pt films.
- 4. Thus, it can be concluded that carbon nanotube network films and their composite films are a feasible alternative flexible, roll-to-roll depositable DSC CE material.

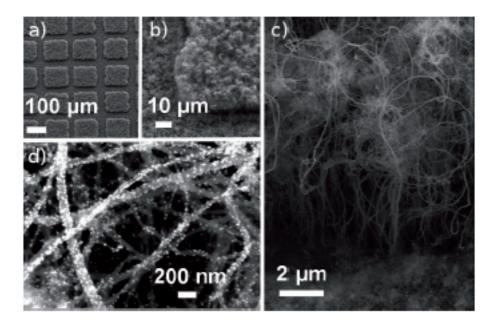


Figure 3: Scanning electron microscope images at different resolution of multiwalled carbon nanotube (MWCNT) forest.

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4. Photonic crystals for light trapping in solar cells

PhD-thesis by Jo Gjessing, IFE, 2012

Abstract

Solar energy is an abundant and non-polluting source of energy. Nevertheless, the installation of solar cells for energy production is still dependent on subsidies in most parts of the world. One way of reducing the costs of solar cells is to decrease their thickness. This will reduce material consumption and, at the same time, unlock the possibility of using cheaper lower quality solar cell material. However, a thinner solar cell will have a higher optical loss due to insufficient absorption of long wavelength light. Therefore, light-trapping must be improved in order to make thin solar cells economically viable.

In this thesis I investigate the potential for light-trapping in thin silicon solar cells by the use of various photonic crystal back-side structures. The first structure I study consists of a periodic array of cylinders in a configuration with a layer of silicon oxide separating the periodic structure from the rear metal reflector. This configuration reduces unwanted parasitic absorption in the reflector and the thickness of the oxide layer provides a new degree of freedom for improving light trapping from the structure. I use a large-period and a small-period approximation to analyze the cylinder structure and to identify criteria that contributes to successful light-trapping.

I explore the light-trapping potential of various periodic structures including dimples inverted pyramids, and cones. The structures are compared in an optical model using a 20 m thick Si slab. I find that the light trapping potential differs between the structures, that the unit cell dimensions for the given structure is more important for light trapping than the type of structure, and that the optimum lattice period does not differ significantly between the different structures.

The light-trapping effect of the structures is investigated as a function of incidence angle. The structures provide good light trapping also under angles of incidence up to 60 degrees. The behavior under oblique incidence angles can to a large degree be predicted by considering the number of escaping diffraction orders which may easily be found from the grating equation.

In addition to the well-known structures mentioned above I also introduce novel lighttrapping structures. I use these structures to investigate what level of light trapping that may be achieved by freely selecting the unit cell geometry. The best light trapping is achieved for structures with low symmetry in their unit cells. The light confinement of one such structure even exceeds the Lambertian light trapping for normal incident light. Lambertian light trapping assumes total randomization of light inside the absorbing material. From geometric optics considerations such a structure will provide the maximum achievable light trapping within a dielectric slab. The Lambertian limit is independent of incidence angle and is therefore valid for isotropic illumination.

To experimentally study light trapping from periodic structures, and moreover to compare with our numerical simulations, we had periodic cylinder arrays fabricated by photolithography. The samples were divided into small blocks of cylinder arrays where lattice geometries and lattice periods varied between the blocks. The measured reflectances from the different blocks are in qualitative agreement with the numerical simulations. A quantitative comparison, on the other hand, is difficult due to the small size of the structured areas.

I have also been a part of a team at IFE investigating fabrication methods which may be better suited than photolithography for low-cost fabrication of photonic crystals for solar cells. These methods comprise nanoimprint lithography on very thin Si substrates and selfassembled structures using nanospheres. The work focused mainly on control and understanding of the fabrication methods. My contributions to this work were in transfer of the nanoimprinted structures from the resist to the substrate and the subsequent analysis, and in discussions and optical measurements of the self-assembled structures.

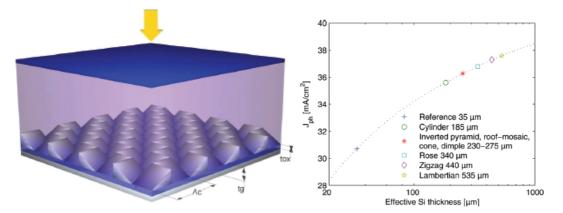


Figure 4: Solar cell model of with advanced low symmetry periodic structure (left). Photogenerated current and effective silicon thickness for 20 µm thick solar cells with different light trapping structures (right).

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- 5. J. Gjessing, A. Sudbø, and E. S. Marstein, "2-D Blazed Grating for Light Trapping in Thin Silicon Solar Cells," in Optics for Solar Energy, Tucson, USA (2010)
- 6. J. Gjessing, E.S. Marstein, A. Sudbø, "2D back-side diffraction grating for improved light trapping in thin silicon solar cells", Optics Express, Vol. 18 (2010)
- J. Gjessing, E.S. Marstein, A. Sudbø, "Modelling of light trapping in thin silicon solar cells with back side dielectric diffraction grating", 24th EU PVSEC, Hamburg, Germany (2009)
- 8. J. Gjessing, A. S. Sudbø, E. S. Marstein, "Comparison of light trapping in diffractive and random pyramidal structures", presented at the 26th EU PVSEC, Hamburg, Germany, 5-9 Sept., section 3AV.3.3, 2011.

5. Multijunction solar cells with subcells based on germanium

PhD-thesis by Nikolay A. Kalyuzhnyy, IOFFE, 2011

This PhD thesis is written in Russian.

The PhD thesis consists of five chapters, introduction, conclusion and list of references. It contains 218 pages including 61 figures and 6 tables. The list of references contains 155 items. The main results of the thesis were presented in 28 publications, including 11 journal papers and 17 proceedings of international and Russian conferences.

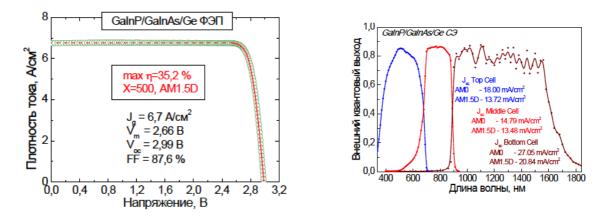


Figure 5: *Current voltage curve (left) and quantum efficiency curve (right) for triple junction GaInP/GaInAs/Ge solar cell.*

6. Formation of Properties of CuInSe and Cu ZnSn(S,Se) Monograin Powders Synthesized in Molten KI

PhD-thesis by Kristi Timmo, TTU, 2011

Abstract

This thesis is focused on the research of regularities of formation of CuInSe₂ (CISe) and Cu₂ZnSn(S,Se)₄ (CZTSSe) monograin powders in liquid potassium iodide (flux). The variation of elemental composition, chemical surface treatment and doping with sodium were used to modify absorber materials properties for monograin layer solar cells (MGL).

The developed CuInSe₂ and Cu₂ZnSn(S,Se)₄ powders were characterized by EDS, SEM, XRD, ICP-MS, XPS, Raman, polarographic analyses and photoluminescence spectroscopy. The monograin powders were used as absorber materials in monograin layer solar cells. The solar cells were characterized by the dark and light current-voltage (I-V), capacitance-voltage, QE and by V_{0c} vs. T measurements.

In the growth process of monograin powders the chemical nature of the liquid (molten) phase of the used flux material impacts the powder crystals growth parameters and properties of the obtained absorber materials. It was found that the growth of powder crystals can be described by the formula: $d_m \sim t_{1/n} exp(-Ed/kT)$. From the Arrhenius plot of the median grain diameter d_m the activation energy for linear crystal growth $E_d = 0.25 \pm 0.05$ eV and from the time dependence of the median grain diameter $d_m \sim t$ at constant temperature the power of the time dependence of crystal growth $1/n = 0.25 \pm 0.06$ and $n = 3.9 \pm 0.93$ were determined. The value of $n = 3.9 \pm 0.93$ indicates that mass diffusion through the liquid phase and sintering of formed grains by material surface diffusion were dominating in the growth process of monograin powder crystals. Crystals of CuInSe2 grown in KI flux had a shape of polyhedrons with smooth facets. By variation of the Cu/In ratio (0.5 - 1.1) in initial Cu-In alloys the area of single-phase CuInSe2 was determined to be between 1>Cu/In>

The processes of the synthesis and isothermal growth of CuInSe₂ monograin powders proceed at elevated temperatures in KI as a flux material and lead to the doping of the grown materials with iodine and potassium (also with Na as impurity in KI) from the flux. The doping with K and Na influences the surface composition, the defect structure and electrical and optical properties of the materials. The peak position of the PL band of Na doped CISe powders shifted depending on the Na doping level and showed the maximum energy when sodium concentration was $1\text{Å}\sim10_{19}$ at/cm₃. The same material had the highest carrier concentration $2\text{Å}\sim10_{17}$ cm-3. The Na doping level of the absorber material had strong influence on the solar cell parameters and the added sodium concentrations $3\text{\AA}\sim10_{18}$ at/cm₃ resulted in the highest open-circuit voltage and fill factor values.

In the case of Cu₂ZnSn(S,Se)₄ growth in molten KI the bulk and the surface compositions of formed CZTSSe crystals were found to be non-identical. This difference in bulk and surface compositions is caused by the different solubilities of the precursors in the molten flux. As a result, different precursor components precipitate out from the flux during the cooling period onto the surface of the grown crystals. The influence of different chemical treatments of powder crystals on the chemical composition of crystals surface was studied to control the surface composition and to improve the parameters of the Cu₂ZnSn(S,Se)₄ monograin layer solar cell. The analysis of the leaching solutions showed that tin and chalcogen can be removed preferably by HCl etching. The leaching with KCN leads to the removal of Cu, Sn and chalcogen from the surface. From the XPS measurements we found that etching with 1% Br₂ in methanol resulted in Sn-rich material surface. The combination of chemical treatments (1% Br₂-MeOH + 10% KCN) resulted in Cu₂ZnSn(S,Se)₄ monograin layer solar cells with the highest values of parameters.

It was shown that monograin powder technology in the use of KI flux enables us to grow Cu₂ZnSn(Se_{1-x}S_x)₄ materials with homogeneous composition in the region of sulfur content x = 0 to x = 0.85. The increasing of sulfur content in Cu₂ZnSn(S,Se)₄ monograin powder absorber materials led to the increase of the forbidden band of material and improved the values of open circuit voltages of MGL solar cells. Solar cell structures based on monograin powders with the concentration ratio of 85 mole% sulfur to 15 mole% selenium yielded in the highest values of V_{0c} = 660mV. The Cu₂ZnSn(S,Se)₄ solid solution with 75 mole % sulfur and 25 mole % selenium gave the highest parameters of solar cell V_{0c} = 622 mV, I_{sc} = 15.87 mA/cm₂, FF = 60 %, η = 5.9 %.

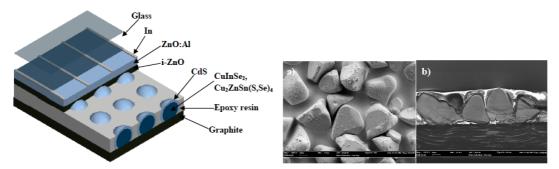


Figure 6: Schematic of a monograin CIGS cell (left). Scanning electron microscope image of CIGS monograin particles (right).

Papers:

- K. Timmo, M. Altosaar, M. Kauk, J. Raudoja, E. Mellikov, CuInSe₂ monograin growth in the liquid phase of potassium iodide. Thin Solid Films, Vol. 515 (2007) 5884-5886.
- M. Kauk, M. Altosaar, J. Raudoja, K. Timmo, M. Grossberg, T. Varema, E. Mellikov, Growth of CuInSe₂ monograin powders with different compositions, Mater. Res. Soc. Symp. Proc. Vol. 865 (2005) 463-469.
- K. Timmo, M. Altosaar, J. Raudoja, E. Mellikov, T. Varema, M. Danilson, M. Grossberg, The effect of sodium doping to CuInSe₂ monograin powder properties. Thin Solid Films, Vol. 515(2007) 5887-5890.
- K.Timmo, M. Altosaar, J. Raudoja, M. Grossberg, M. Danilson, O.Volobujeva, E.Mellikov, Chemical etching of Cu₂ZnSn(S,Se)₄ monograin powder, 35th IEEE Photovoltaic Specialists Conference, Honolulu, Hawaii, June 20-25, 2010: Conference Proceedings 1982 - 1985.
- M. Altosaar, J. Raudoja, K. Timmo, M. Danilson, M. Grossberg, J. Krustok and E. Mellikov, Cu₂Zn_{1-x}Cd_xSn(Se_{1-y}S_y)₄ solid solutions as absorber materials for solar cells, Physica Status Solidi A - Applications and Materials Science, 205 (1) (2008) 167-170.
- K. Timmo, M. Altosaar, J. Raudoja, K. Muska, M. Pilvet, M. Kauk, T. Varema, M. Danilson, O. Volobujeva, E. Mellikov, Sulfur-containing Cu₂ZnSnSe₄ monograin powders for solar cells, Solar Energy Materials & Solar Cells 94 (2010) 1889-1892.

7. Life-Time studies for Dye-sensitized Nanostructured Solar Cells

PhD-thesis by Anders Rand Andersen, 2011

Institute: Danish Technological Institute & Institute of Technology and Innovation, University of Southern Denmark

Abstract

This study is on dye-sensitized solar cells (DSC) which are a new class of photovoltaic devices with the potential to rival conventional solar cells. DSC can be manufactured from low cost materials, and champion cells have efficiencies above 11 % under standard conditions, although the thermal stability in some cases have shown to be an issue for such cells. Especially, it is often found that DSC heated to 85 C will loose 20-50 % of the initial efficiency depending on the specific design and material quality. Some groups claim to be able to produce DSC that will loose less than 10 % of the initial efficiency even after 1000 hours at 85 C.

In this work, we aimed at finding the major reasons for limited thermal stability of DSC. The main work packages have involved analyzing the performance, the photocurrent generation and the electrochemical impedance of fresh and heated laboratory DSC. The work is based on analysis of chemicals extracted from heated DSC. An important result is

that various high performance dye molecules can react with species in the liquid electrolyte of the DSC at elevated temperatures, and hence form substitution products. Knowing this, we could interpret the photo current generation and impedance data. The found substitution products was then synthesized, and used as sensitizers in otherwise fresh DSC. This means that we had DSC containing 100% artificially degraded dyes, and these could then be analyzed.

It is found that heated cells and cells containing degraded dye show similar charge transport and recombination characteristics. Furthermore, the photocurrent generation and the performance data are closely correlated for the two types of cells. The work thus show that the weak point regarding thermal stability of high performance DSC is closely related to the loss of thiocyanate ligands in the champion dyes, which is a consequence of the high temperature reaction.

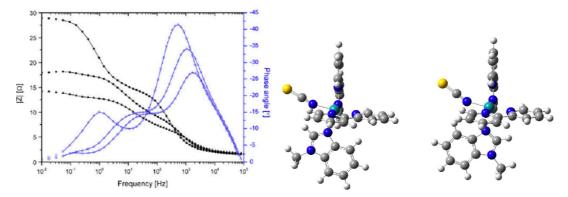


Figure 7: Impedance spectroscopy curves for dye-sensitized solar cells (DSC) before and after heat treatment (left). Simulation showing two possible forms of thermal degradation products from a DSC (right).

Papers:

- P. T. Nguyen, A. R. Andersen, E. M. Skou, T. Lund Dye stability and performances of dye-sensitized solar cells with different nitrogen additives at elevated temperatures – Can sterically hindered pyridines prevent dye degradation? Solar Energy Materials & Solar Cells 94 (2010) 1582-1590
- Nguyen, P. T., Lam, B. X. T., Andersen, A. R., Hansen, P. E. and Lund, T. (2011), Photovoltaic Performance and Characteristics of Dye-Sensitized Solar Cells Prepared with the N719 Thermal Degradation Products [Ru(LH)₂(NCS)(4-*tert*butylpyridine)][N(Bu)₄] and [Ru(LH)₂(NCS)(1-methylbenzimidazole)][N(Bu)₄]. Eur. J. Inorg. Chem., 2011: 2533–2539
- A. R. Andersen, J. Halme, T. Lund, M. I. Asghar, P. T. Ngyuen, K. Mietunnen, E. Kemppainen, O. Albrektsen Charge transport and photo current generation characteristics in dye solar cells containing thermally degraded N719 dye molecules, *J. Phys. Chem. C*, **2011**, *115* (31), pp 15598–15606

Network strengthening activities

To further strengthen and expand the Nordic PV network to include the Baltic region, the following types of network activities have been arranged:

Hands-on workshop: This workshop allows the participants to gain deep understanding into solar cell fabrication methods both through theoretical insights and by going through the different processing steps in the lab. In this workshop the number of participants is limited to allow good interaction between participants and lecturers. The PhD students gain valuable experience and the workshop is excellent for transfer of knowledge.

In-depth workshop: In these workshops the topic is focused around a particular challenge for the PV community. Specialists within the fields are invited to these workshops to present their research.

Conference: Conferences are broader in scope than in-depth workshops and attract a wider audience. The conference included submission of abstracts, oral and poster sessions and invited speakers. Conferences give the opportunity to make connections outside ones particular field of expertise.

The different networking activities have also been accompanied by tours showing the facilities of adjacent labs or PV factories. The participants have been given tours in both RECs silicon solar cell factory in Narvik and at Solibros Research CIGS thin film factory in Ultuna. The social activities during these seminars have also been important in order to build relationships between the different participants. The social activities have amongst others included train ride with Ofotbanen with Rallarfest and reception in the main building of the Estonian Academy of Sciences in the old town of Tallinn.

The networking activities have included participants from all participating research institutions and from companies working with solar electricity. The exception is the hands on workshop that were held exclusively for the PhDs involved in this project.

Type of event	Title of event	Date(s), host institution, country	Number of participants	Accompanying activities
In depth workshop	2nd Nordic Workshop on Crystalline Silicon Solar Cells	5-6 March 2008, IFE, Norway	28	Visit at REC factory in Narvik. Train ride with Ofotbanen
In depth workshop	Nordic seminar on modeling of CIGS devices	16. October 2008, UU, Sweden	50	Visit at Solibro research factory
Hands-on workshop	Hands on seminar on Crystalline silicon solar cells	24-27 November 2008, IFE, Norway	6	Common dinner
Conference	3rd Nordic PV Conference	18-19 May 2009, Tallinn, Estonia	75	Lab tour at facilities of TTU. Dinner in old town.
In depth workshop	Nordic Photovoltaic workshop on Stability and Encapsulation	23-24 May, 2011	18	Common dinner

The networking events are listed in the table below:

Next year a closing general seminar is planned with focus on the obtained results during this project. This will also be an arena for discussion of possible future joint research projects.

The programs for the different events are shown below.

2nd Nordic Workshop on Crystalline Silicon Solar Cells

Location: Høgskolen i Narvik, Lodve Langesgt.2, March 5th - 6th 2008

Program Wednesday March 5th 2008

Afternoon session 1200-1700 Registration and lunch About NCoE in PV (Arve Holt, IFE,Norway)

Light trapping (Arve Holt, IFE)

Light trapping by porous silicon (Sean Erik Foss, IFE, Norway) Polariton enhanced absorption in solar cells (Ingve Simonsen, NTNU, Norway) Photonic crystals for photovoltaic applications (Jo Gjessing, IFE, Norway)

Break (30 min)

Advanced characterization for solar cells (Charlotte Platzer-Björkman, Uppsala University) Carrier density imaging (Martin Schubert, Fraunhofer ISE, Germany) Shunt and Micro Crack Characterization of Multi Crystalline Silicon Wafers (Dr. Tobias Boström, Norut Technology AS, Norway)

1900 Excursion and dinner on the spectacular Ofotbanen in the Navvy spirit

Program Thursday March 6th 2008

Morning session 0900-1300

Alternative solar cell structures (Andreas Bentzen, REC)

Multi-junction solar cells (Nikolay Kalyuzhnyy, IOFFE, Russia) Silicon-based 3rd generation solar cells –status (Erik Stensrud Marstein, IFE, Norway) HIT solar cells (Lode Carnel, REC Scanwafer AS, Norway)

Break (30 min)

Contacting technologies (Roy Antonsen, REC)

Transparent conductive oxide materials (Marika Edoff, Uppsala University, Sweden) Electroless Silver Plating of Screen Printed Front Grid Fingers as a Tool for Enhancement of Solar Cell Efficiency (Eckard Wefringhaus, ISC-Konstanz, Germany)

Lunch 1300-1400

14.00

Presentation by REC ScanCell

The expansion of the site and Introduction to guided tour

15.00 - 18.00

Guided tour of the new 180 MW REC ScanCell factory End

Nordic seminar on modelling of CIGS devices

Time: Thursday 16/10 2008 Location: Häggsalen, ground floor, Ångström Laboratory 9.30-10.00 Coffee

Morning session: Modelling of cells and modules

10.00 Marika Edoff, UU Welcome	
10.15 Jim Sites, Colorado State University	
"Simulations of CIGS Solar Cells"	
10.45 Ulf Malm, UU	
"Simulating Material Inhomogeneities and Defec	ets in CIGS Thin-film Solar Cells"
11.15 Uwe Zimmermann, UU	
"Modelling and simulation of CIGS modules"	

Lunch 12-13

Afternoon session: Alternative buffer layers - characterisation and modelling

13.15 Charlotte Platzer-Björkman, UU

	"Alternative buffer layers - overview and status"
13.45	Jonas Pettersson, UU
	"Electrical characterization of devices with (Zn,Mg)O buffer layers"
14.15	Pawel Zabierowski, Warsaw University of Technology
	"Modelling of fill factor losses in CIGSe-based solar cells"
14.45	Marika Edoff, Solibro

"Solibro today and introduction to lab tour"

Visit to Solibro

15.15	Transfer to Solibro Research, Ultuna
15.30	Coffee and lab tour
16.30	Transfer to Ångström lab and Uppsala train station

Program Nordic Hands-On Workshop on Crystalline Silicon Solar Cells

Location: IFE, Date: 24-27 November 2008

Monday November 24^h (1100-1600)

Introductory lecture and safety roles Sample preparation Damage removal and texturing Scanning electron microscopy (SEM) and infinite focus microscopy

Workshop dinner in the evening

Tuesday November 25th (0900-1600)

Short process introduction lecture on emitter formation Diffusion source deposition Diffusion and oxidation Sheet resistance mapping

Wednesday November 26th (0900-1600)

Short process introduction lecture on ARC SiNx ARC deposition Spectral response and ellipsometry measurements Screen Printing

Thursday November 27th (0900-1600)

Short process introduction on contacting of solar cells Screen printing and firing IV measurements and introduction into LBIC measurements Closing session

3rd Nordic PV Conference

Location: Tallinn, Estonia. Date: 18-19 May 2009 Arrival Sunday, May. 17, 2009 Accommodation in the hotel "Reval Hotel Central" 20.00 Welcome cocktail – Reval Hotel Central

Monday, May 18

8.40 - Departure from the hotel. Bus transfer to Tallinn University of Technology, room VII
226, main building, Assembly Hall, Ehitajate tee 5, Tallinn
9.00 - registration and welcome coffee

Session: THIN FILM PV

Prof. E.Mellikov, Dept of Material Science, Tallinn University of Technology
Opening of the Conference
Prof. Enn Mellikov, Dept of Material Science, Tallinn University of Technology
Welcome address
Prof. Rein Vaikmäe, Vice-Rector for Research, Tallinn University of Technology
Welcome address
Einari Kisel, Deputy Secretary General of Energy, Ministry of Economic Affairs and
Communications, Estonia

9.40-9.45	Arve Holt, Head of the Nordic CoE
9.45 - 10.25	Design Rules for Heterojunction Solar Cells
	Roland Scheer Helmholtz-Zentrum Berlin GmbH, Germany
10.25 - 10.55	Cutting edge research and recent results, Ångström Solar Center
	Marika Edoff, Uppsala University, Sweden
10.55 - 11.20	COFFEE BREAK and poster session
11.20 - 11.40	Powder Approaches to Solar Cells
	Dieter Meissner, E. Mellikov Tallinn University of Technology, Estonia
11.40 - 11.55	Chemical Bath Deposited ZnS Thin Films for CuInS2 Solar Cells
	Kaia Ernits, et al, Tallinn University of Technology
11.55 - 12.10	Morphology, electrical and optical characterization of oriented CuIn3Se5 films
	prepared by high vacuum evaporation technique
	Kristjan Laes et al. Tallinn University of Technology
12.10 - 12.25	Growth of ultra-thin TiO2 films by spray pyrolysis on different substrates
	I. Oja-Acik et al. Tallinn University of Technology
12.25 - 12.40	Sulfur-containing Cu2ZnSnSe4 monograin powders for solar cells
	Kristi Timmo et al. Tallinn University of Technology
12.40 - 12.55	Atomic Layer Deposition: an Advanced Technology for the Processing of
	Photovoltaic Thin Film Materials and Structures Based Thereupon
	Lauri Niinistö et al, Helsinki University of Technology, Finland
13.00 - 14.00	LUNCH and poster session
14.00 - 15.00	Visit to laboratories

Session: OTHER

Chair:	prof. Arve Holt, Institute for Energy Technology, Norway
15.10 - 15.25	Infrared to visible upconversion luminescence in oxide materials
	Edita Garskaite et al. Norwegian University of Science and Technology
15.25 - 15.40	High penetration of RE in a future power system with Photovoltaic as Virtual Power
	Plants
	Jesper Bergholdt Soerensen, Energinet.dk, Denmark
15.40 - 15.55	Multi-junction solar cell structures grown by MOCVD with in-situ investigations
	Nikolay Kalyuzhnyy, S.A. Mintairov, V.M. Lantratov, Ioffe Physical-Technical
	Institute, Russian Academy of Sciences
15.55 - 16.10	High-Concentration Approach
	Valery Rumyantsev, Ioffe Physical-Technical Institute, Russia
16.10 - 16.25	Modelling of back-side diffraction gratings applied for light trapping in silicon solar cells
	Jo Gjessing et al. Institute for Energy Technology, Norway
16.25 - 16.55	COFFEE BREAK and poster session
16.55 - 17.10	The battle of light – semi-transparent PV panels in glass facades Hanne Lauritzen,
	Danish Technological Institute, Denmark
17.10 - 17.25	Excited State Dynamics in Light Harvesting Materials: What can we learn via
	coherent multidimensional spectroscopy?
	Tõnu Pullerits, Lund University, Sweden
17.30	Transfer to the hotel
18.45	Departure from hotels
19.00 - 21.30	Reception at the main building of the Estonian Academy of Sciences (Kohtu Str 6)
Tuesday, May 1	
9.30 -	Departure from the hotel. Bus transfer to Tallinn University of Technology, main
	building, Assembly Hall, Ehitajate tee 5, Tallinn
Session: DYE	
Chair:	Prof. D. Meissner, Dept of Material Science, Tallinn University of Technology
10.00 - 10.50	Status of Industrialization of Dye Solar Cells for BIPV Applications
	Keith Brooks, Greatcell Solar SA, Switzwerland
10.50 - 11.05	Customized DSC Modules
11.05 11.00	Kasper Nørgaard et al., Danish Technological Institute
11.05 - 11.20	The current enhancing effect of carbon nanotubes on dry ionic liquid electrolyte dye
	solar cells
	K. Aitola, M. Toivola, J. Halme, P. Lund Helsinki University of Technology, Finland

11.20 - 11.50	COFFEE BREAK and poster session
11.50 - 12.05	Linking photovoltaic performance and physicochemical cell parameters in dye sensitized solar cells
	Anders Rand Andersen, Danish Tecnological Institute, Denmark
12.05 - 12.20	Analysis of degradation issues for improved dye sensitized solar cells
	Muhammad Imran Asghar et al. Helsinki University of Technology; Finland
12.20 - 12.35	Degradation chemistry of N719 and Z-907 dyes at elevated temperatures
	Torben Lund et al. Roskilde University,
12.35-12.50	The role of Hydrogen in ITO films
	Jeyanthinath Mayandi et al. Institute for Energiteknikk, Norway
12.45 - 13.45	LUNCH and poster session
14.00 - 15.00	Poster Session
15.00 - 15.30	Closing of the Conference
15.45	Bus transfer to the hotel

Nordic Photovoltaic workshop on Stability and Encapsulation

Location: Helsinki, Finland. Date: 23-24 May 2011

23rd May 2011

12:00-14:00	Registration
12:30-13:30	Lunch
Chairman (Prof.]	Peter Lund)
14:00-14:15	Welcome and Introduction
14:15-15:45	Invited speaker (Dr. Oreski Gernot, PCCL, Austria) "PV encapsulation and
	degradation behavior of common PV encapsulation materials, Qualification of
	new polymeric materials for use in PV modules and Lifetime modeling"
15:45-16:15	Discussion and Coffee refreshment
16:15-16:45	Key note speaker (Prof. Lars Stolt, Solibro, Sweden/Germany) "Encapsulation for
	thin film PV modules: State of the art and directions for R & D"
16:45-17:00	Discussion
17:00-17:15	Short Talk 1 (Imran Asghar, Aalto University, Finland) "Color analysis technique
	to study the stability of PV cells – case dye solar cells"
17:15-17:30	Short Talk 2 (Päivikki Repo, Aalto University, Finland) "Stability of Al2O3
	passivation in crystalline Si solar cells"
17:15-17:45	Discussion and Summary of the 1 st day
19:00- 21:00	Workshop Dinner and other activity
24 th May 2011	
Chairman (Dr. Ka	ati Miettunen)
09:00 - 10:30	Invited speaker (Prof. Torben Lund, Roskilde University, Denmark) "Stability of
	dye solar cells in general and degradation chemistry"
10:30-11:00	Discussion and Coffee refreshment
11:00-11:45	Key note speaker (Dr. Kati Miettunen, Imperial College London) "Stability issues of
	flexible dye solar cells"
11:45-12:00	Discussion
12:00-13:00	Lunch
13:00-13:15	Short Talk 3 (Kerttu Aitola, Aalto University, Finland) "Stability issues of flexible
	carbon nanotubes based dye solar cells"

13:15-13:30	Short Talk 4 (Anders Rand Andersen, University of Southern Denmark)
	"Monitoring new PV technologies"
13:30-13:45	Discussion and Summary of the 2 nd day

14:00 Adjourn

Mobility of scientific personnel

In addition to the above-mentioned network activities there have also been exchange of students and scientific personnel between institutions.

- Charlotte Platzer-Björkman, at that time post doc at UU, spent one year at IFE doing research and supervising PhD students at IFE. Platzer-Björkman was also the opponent to Kristi Timmo of TTU on her thesis defence.
- Jonas Petterson from UU spent about a month at IFE to learn more about Silvaco simulations.
- There has also been good cooperation the groups working on dye-sensitized solar cells. Anders Rand Andersen from DTI and SDU visited Aalto University (former Helsinki University of Technology) and their cooperation lead to several joint papers between the two institutions.
- Kerrtu Aitola from Aalto University spent parts of her final year as PhD student at UU.

The project had initially even higher ambitions for exchange of scientific personnel. However, due to the different topics and focus areas of the different labs, it was sometimes difficult to find a good match for exchange.

Impact on PV R&D in the Nordic and Baltic region

The PV industry has been through an incredible change since the start of this project. In 2007 a total amount of 3 GW was installed bringing the total installed capacity up to almost 10 GW. In 2012 alone more than 30 GW of PV panels was installed bringing the total up to more than 100 GW. However, the actually PV production capacity have risen even faster during the same period, creating a significant oversupply leading to a massive reduction in solar module selling prices. Between 2009 and 2012 the solar module prices have dropped by a staggering 75 percent. As a consequence several PV manufacturers have gone bankrupt and expenses have been dramatically reduced in all parts of the value chain including R&D. In the same time period the PV landscape has changed completely; European and US manufacturers have been hit the hardest and production have moved east to countries like China, Taiwan, Singapore and Malaysia. Only in recent months have there been signs of recovery and the future starts to look brighter. On the positive side, the price reductions have lead to cheaper solar electricity and today PV has reached grid parity in about 100 markets around the world⁶.

Also the Nordic companies involved in this project have gone through difficult times. However, looking at all the companies involved in this project, Elkem Solar (Norway), REC ASA (Norway), Solibro research AB (Sweden), Topsil A/S (Denmark), Energinet.dk (Denmark), Luvata (Finland), everyone of them are still working with PV today. That is quite remarkable considering the number of bankruptcies the last few years. It is difficult to tie such an achievement up against a particular factor, but it is possible that these companies have survived because they have put a high priority on R&D, which is particularly important in the PV business due to its rapidly evolution. We also see now that several new companies are following and attracting new investments. Recently we have seen several new companies forming in Norway and Sweden and the number of PV companies in Norway today is twice as high as in 2005⁷. This would not be possible without access to qualified personnel and centers of competence.

A few concrete examples of impact on R&D in the Nordic and Baltic region: One of the PhD students in this project, Anders Rand Andersen from DTI and SDU, has started a company that delivers technology towards the PV system market. The company, EmaZys⁸, delivers technological solutions to locate flawed modules in a larger PV system. The technological solution is related to the work performed in his PhD thesis.

⁶ <u>http://reneweconomy.com.au/2013/graph-of-the-day-solar-grid-parity-in-102-countries-</u> <u>39133</u>

¹ http://www.tu.no/kraft/2013/09/27/antall-norske-solenergiselskaper-har-doblet-segsiden-2005 8

www.emazys.com

The work of PhD student Jo Gjessing have been followed up by another large project (ISP) at IFE and there has been a close cooperation between the projects leading to several journal papers and also one PhD (Jostein Thorstensen). Additionally this work has generated press coverage worldwide⁹. The ISP project will be finalized this fall.

The company Crystalsol¹⁰, formed in 2008, is based on some of the findings of PhD student Kristi Timmo at TTU. Moreover, her work strongly influenced two other PhD students to follow; Olga Volobujeva, Maarja Grossberg, and their thesis are indirect results of this project.

These are just a few examples of positive spill over effects of the NCoE in PV. Perhaps most impressive of all is the fact that all seven PhD students involved in this project have successfully defended their thesis. That implies that the research institutions have contributed with good research projects and supervision, and that they have been able to attract clever people.

A new trend that has emerged since the start of this project is an increasing installation rate of PV in the Nordic markets. The use of PV has become more relevant than ever as a consequence of rapidly falling PV module prices the last few years. In Denmark the marked for PV have exploded, and Sweden seem to follow. Norway and Finland are some steps behind, but also here the future is likely to be sunny. This part of the value chain has not been a part of this project, but it might be of interest for future projects.

⁹ Here follows five out of more than 30 paper and online versions of the story light trapping using microbeads for texturing.

⁻ Apollon 1/2013 side 20 "Neste generasjons solceller" paper version

^{- 29/1:} TV2-nyhetene <u>http://www.tv2.no/nyheter/innenriks/slik-lurer-de-sollyset-til-aa-lage-mer-stroem-3976860.html</u>

^{- 29/1-2013} Physorg http://phys.org/news/2013-01-solar-cells-sunlight-microbeads.html

^{- 31/1:} photonics http://www.photonics.com/Article.aspx?AID=52973

⁻ PHOTONICS SPECTRA Volume: 47 Issue: 4 Pages: 66-66 Published: APR 2013

¹⁰ http://www.crystalsol.com/engl/news/news.html