

**MASTER THESIS**

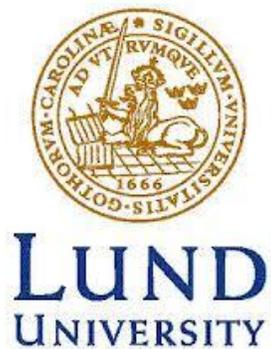
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**IDENTIFICATION OF PROCESS INDUCED DEFECTS  
AFFECTING THE PERFORMANCE OF NANOWIRE  
BASED SOLAR CELLS BY SPATIALLY RESOLVED  
PHOTOCURRENT MEASUREMENTS**

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## i ABSTRACT

Solar power clearly has one of the greatest potential among renewable energy but a big setback is that it is still relatively expensive. Engineering of materials on a nanoscale, e.g. the growth of nanowires makes it possible to make semiconductor-materials with better optical properties while using less material than for traditional bulk semiconductors. This means that nanowire based solar cells has the potential to be cheap to produce while they also could reach high efficiencies possibly making solar cells on a large scale a reality. Lund University is one of the best in the world in growing rows of high quality nanowires and has produced a record solar cell based on InP nanowires with an efficiency of 13.8% in 2012.

During this project, a photocurrent measurement technique that can resolve the photocurrent on a solar cell has been further developed and evaluated. There has also been several measurements and investigations on a sample called SCIL 51-84 that had 7 III-V InP nanowire solar cells.

The work has led to identification of local defects in material and processing, and an evaluation technique that in this project is called *inverted images* and may lead to a safer and faster way of detecting abnormalities on these nanowire-based solar cells. Four kinds of defects were investigated and two of these could be removed using reactive ion etching with oxygen plasma. Removal of the optical defects led to an increased performance with about 40% compared to before. The limitations and suggestions on further development of the setup are also discussed.

## ii SAMMANFATTNING

Solenergi har en utav den överlägset största potentialen bland förnyelsebar energi men utgör bara en liten del av den globala energitillförseln bland annat på grund av att elektricitet från solceller kostar mycket per kWh. Nanotrådssolceller, en ny typ av solceller med bra optiska förmågor, har potential att nå höga verkningsgrader. Samtidigt används mindre halvledarmaterial vilket gör det möjligt att dra ned på materialkostnader vilket gör att det kan bli mer ekonomiskt motiverat att producera solceller i stor skala.

Nanotrådar är trådliknande strukturer som är växta atom för atom. Provet jag utförde mätningar på hette SCIL 51-84 och trådarna på det hade en diameter som var cirka 200 gånger tunnare än ett hårstrå. Lunds universitet är en av de i bästa i världen på att växa nanotrådar av hög kvalite i jämna rader och har år 2012 lyckats producera en rekordcell med verkningsgraden 13.8% baserad på InP-nanotrådar.

Under detta examensarbete har jag fokuserat på att vidareutveckla och utvärdera en uppställning för mätning av fotoströmmar. Det har även gjorts flera mätningar på SCIL 51-84 som hade 7 stycken InP nanotråds solceller.

Arbetet ledde till identifiering av defekter i material och tillverkning och en utvärderingsteknik som i detta arbete kallas för *inverted image* som skulle kunna göra det snabbare och säkrare att upptäcka oplanerade höjdvikelser på nanotrådssolceller.

Fyra sorts defekter undersöktes och två av dessa kunde tas bort med syreplasma-etsning (reactive ion etching with oxygen plasma). De optiska defekterna som kunde tas bort visade sig vara resist på solcellen. När defekterna etsades bort blev solcellen mer uniform och verkningsgraden ökade med 40 % jämfört med innan etsning.

Även begränsningar och förslag på förbättringar i mätuppställningen av fotoström diskuteras.

### iii NOMENCLATURE

**AFM** = Atomic Force Microscopy

**Al** = aluminium

**Au** = Gold

**DIL** = Dual In Line

**IEA** = International Energy Agency

**InP** = Indium Phosphide

**IPCC** = International Panel on Climate Change

**ITO** = Indium Tin Oxide

**MOVPE** = Metal Organic Vapor Phase Epitaxy

**NW** = Nanowire

**PV** = Photovoltaics

**RIE** = Reactive Ion Etching

**SEM** = Scanning Electron Microscope

**SiO<sub>2</sub>** = Silicon dioxide

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# 1 INTRODUCTION

## 1.1 Background

More effort needs to be done with respect to economic, social, environmental, ecological and political reforms in order to build more sustainable and ecologically adapted societies. These efforts are all part of something called sustainable development.

Sustainable development is defined by the United Nations' Brundtland-report from 1987 as:

*"...a development that meets the needs of the present without compromising the ability of future generations to meet their own needs."* [1]

Something that might be unsustainable is global warming which is caused by the greenhouse effect.

About two thirds of the solar radiation penetrate the atmosphere and reach the surface of the Earth. Long wave infrared radiation leaves the Earth and a part of these are re-radiated by the atmosphere back to Earth. This is called the greenhouse effect and is necessary for much of the life on Earth. Without the greenhouse effect the Earth would have a global mean temperature of  $-18^{\circ}\text{C}$  ( $\sim 255\text{K}$ ) instead of the current  $+14^{\circ}\text{C}$  ( $\sim 287\text{K}$ ). [2]

Global warming has during the last decade been a heavily discussed topic. The idea that greenhouse gases lead to global warming was first put forward in the 1890s by the Swedish chemist Svante Arrhenius. Since then it has been observed that the global mean temperature has increased  $0.8^{\circ}\text{C}$  globally from the 1900s to the beginning of 2000. In comparison, the temperature difference between a warm-period and an ice-age period is  $1-2^{\circ}\text{C}$ . Many researchers claim that such rapid climate change has never happened before and that the main reason is greenhouse gases released by humans. Therefore there is a large scientific consensus that limiting the emission of greenhouse gases is necessary to avoid severe impact on humans and eco-systems. [2][3][4]

Examples of common greenhouse gases released by human establishments and societies are carbon-dioxide, methane, CFCs (ChloroFluoroCarbons) and nitrogen-dioxide. Carbon-dioxide is not the strongest anthropogenic greenhouse-gas, but most of the attention is focused on it since it is responsible for slightly more than 50% of the increase of the global greenhouse effect. [2] Most of the greenhouse-gases are released when burning fossil fuels. The burning of fossil fuels affects not only the emission of greenhouse gases, but is also associated with other environmental problems such as air pollution, photochemical smog and acidification of soil and oceans.

### Various financial instruments of control for a sustainable development

According to IPCC (2012), fossil fuel constitute approximately 85% of the global energy sources today and therefore some experts report that it will be impossible to stop the use of fossil fuels, both politically and economically speaking. Moreover, today's rate of consumption of goods, for example electricity and meat causes a lot of  $\text{CO}_2$ -emission. However some experts are also skeptical of the actual contribution from humans to global warming.

Christian Azar was appointed professor of Energy and Environment at Chalmers University when he was 31 years old, is also a member of the United Nations' IPCC and the Swedish government's commission on sustainable development. [5][6][7] He is certain that it is the use of fossil fuels that drives global warming and also discusses in his book *Power over the climate* (Makten över klimatet) how the global climate goals can be reached.

He also discusses ways to entirely stop fossil fuel usage. Azar says that even though there are uncertainties in the climate-simulations (as in all kinds of science), it would be prudent to decrease the  $\text{CO}_2$ -emissions because then there would be more time to respond in case there are severe environmental catastrophes.

But  $\text{CO}_2$ -abatement isn't entirely about the individual. Based on past history, a combination of financial instruments of control (i.e. tax, electric certificates and emission permits) seems like a necessity to encourage both individuals and companies to control pollution.

Christian Azar states in his book that:

*“No larger environmental issues have been solved by individuals spontaneously changing their behavior. The problems have been solved by governments and parliaments that have passed new laws, economical management measures, prohibitions or other regulations. It is catalyzers, prohibitions against ozone depleting substances and reduced sulfur-content in diesel, that has played the key role, just to name a few examples”* [8]

Klas Eklund, a Swedish economist working with sustainability issues, is on the same track:

*“A possible way to decrease the emissions could be for the government to take measures and do what the market haven’t been able to do, which is to put a price on the CO<sub>2</sub>-emissions.”* [9]

But there are some people thinking that decisions as above would have catastrophic consequences.

The former American republican senator Chuck Hagel once expressed his opinion about the Kyoto protocol:

*“The economic impact would be devastating for the United States. We would see the loss of millions of jobs, entire industries would flee to other countries, our people would face higher fuel costs, higher taxes, leading to lower productivity and a lower standard of living.”* [10]

This might not be true, because according to calculations by the American climate-researcher, Stephen Schneider we will become 10 times wealthier<sup>1</sup> two years later if the Kyoto protocol is followed. In year 2102 if the goals of the Kyoto protocol are reached and in year 2100 if the economy continues as usual. [11] Christian Azar’s opinion is that the real issue is not the large costs but it lies in *how* the costs should be divided. Which countries should be winners and losers? Which companies should be winners and losers when the cost has to be distributed through international agreements and management control measures? That is a political mine-field that decision makers have to face.

In the year 2000 77% of the gasoline-price in Great Britain was tax [12]. This shows how measures have been taken to decrease the usage of petroleum and keep the CO<sub>2</sub> emissions and other pollutions in check. Based on estimations<sup>2</sup> I have made, the cost of producing electricity from solar power<sup>3</sup> in Sweden is<sup>4</sup>: 37 cents/kWh and coal-power<sup>5</sup> 12 cents/ kWh.

Seen from a business perspective, the director of the coal-power plant would not voluntarily give away a competitive advantage of 25 cents/kWh to solar power-plants. Therefore, as Christian Azar is saying, management control measures are necessary, at least in the beginning, to give renewable energy like solar power a chance to become established on the market.

There is a vast amount of strategies in decreasing the pollution of carbon dioxide and it seems that most of these could be put into 3 main categories:

- 
- Lower energy use(by using less electricity, energy-saving lifestyles and limiting the population growth)
  - Use of energy sources with less carbon-emissions(for example, renewable energy sources and alternative energy sources such as hydrogen)
  - Carbon capture and storage(underground, in rock-shelters, in the ocean and other geological formations)

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Existing commercial technologies such as pipelines could be converted as a component for carbon capture and storage usage. Even though it is projected as expensive, it is an attractive solution for large and powerful coal, oil and gas companies. Moreover, legal framework on international agreements needs to be set since there are long-term liabilities related to carbon capture and storage. One of these risks is CO<sub>2</sub> leakage, and many of the other long-term environmental effects of carbon storage are now being evaluated. [13] [14] [15]

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<sup>1</sup> compared to year 1990

<sup>2</sup> see appendix C

<sup>3</sup> polycrystalline solar cells, 13% efficiency, 70% subsidies, based on numbers from Akademiska hus in Lund.

<sup>4</sup> assuming that 1USD = 6.5SEK

<sup>5</sup> mineral-coal(90% coal), 46% efficiency, 7000 operating hours/year

If the carbon storage method is effective, then vehicles driven by bio-fuels for example, can result in a negative contribution of CO<sub>2</sub> and even coal-energy plants could contribute to CO<sub>2</sub> abatement, since 90% of their emissions are captured. [14]

The other two bullet points are related to supply and demand, discussed below.

### **Demand**

The demand side is where a lot of quick improvements could be made. If sustainable products can provide certain reductions they also have to make economic sense as there is no point in making products that people don't want or cannot afford to buy. Examples of decreasing the demand-side are zero carbon houses, encouraging recycling and to live more energy efficient. This is easier said than done because even when a product produced by a company doesn't have a positive impact on the environment for example it is still marketed as if it does and regrettably people who want to be environmentally-conscious buy them without realizing this fact. This is why more guidelines have to be made on a governmental level with counseling from experts.

Sweden is taken as an example. The Swedish energy state agency, Energimyndigheten, estimates that 12-14% less energy could be used in Sweden in the year 2016 compared to what was used in 2009. The energy consultant Sweco claims that half of the energy used in Sweden during the year of 2005 is enough to supply the whole country for a full year in 2030 if a number of political actions are taken<sup>6</sup>. [16][17] However economists warn for a so called rebound-effect, which means that money saved by being energy efficient, will be spent on buying or consuming more things than usual, which means that the energy demand as a whole wouldn't decrease.

### **Supply**

#### Why renewable energy?

The supply side is what many researchers around the world are working with, including everything from bio-fuels to many kinds of renewable energy.

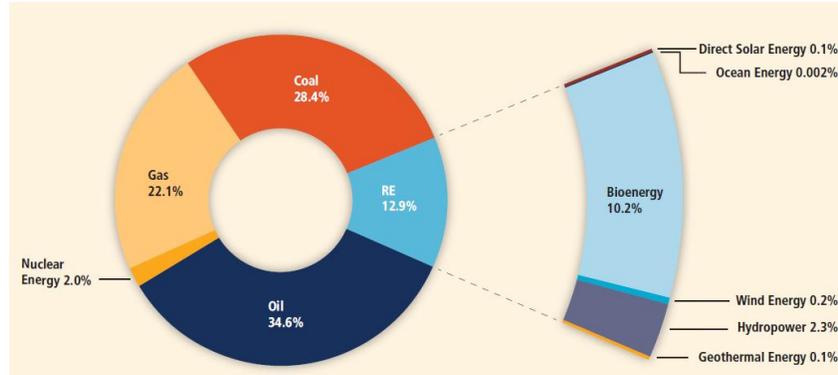
The advantage with renewable energy is the smaller risk of running out of energy supply and that there are few or no greenhouse gas emissions. Renewable energy is also usually low-carbon energy sources. Over its lifetime, solar power (single crystal silicon) emits about 70g CO<sub>2</sub>/kWh whereas a non-renewable energy source such as a modern coal power plant emits over 600g CO<sub>2</sub>/kWh [18].

Sweden has excellent qualities and conditions for adjusting to a renewable energy based society. There are for example large areas of forests, many non-populated areas, a low population density and well developed technology and social welfare. Sweden's target is to have 50% of the energy supply from renewables by 2020 [19].

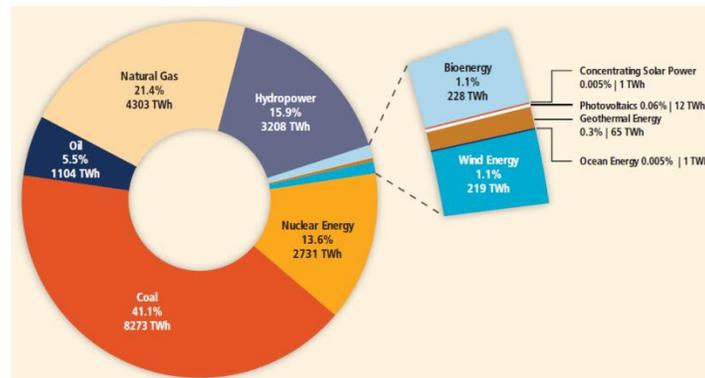
Renewable energy in 2008 constituted 12.9% of the global primary energy supply and 18.5% of the global electricity supply (see fig. 1 and fig. 2).

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<sup>6</sup> a possible scenario as calculated by Sweco, stated that being more energy-efficient would contribute to a 34% reduction and financial instruments of control a 14% reduction for a total of 48% reduction compared to 2005.



**Fig. 1:** Global primary energy supply divided into its shares of energy sources in 2008. Fossil fuel comprised 85.1% and renewable energy 12.9% of the global primary energy supply (IPCC 2012).



**Fig. 2:** Global primary electricity supply divided into its shares of energy sources in 2008. Solar power is currently a small fraction of the global supply (IPCC 2012).

### About solar power

The sun will continue to supply the earth with energy as it does today for about 5 billion more years, thus it can be seen as a renewable source of energy. Since the sun is the driving force creating all weather on Earth, wind power and wave power are other forms of indirect sun-energy.

30% of the sun's energy illuminating the Earth is reflected by the atmosphere or reradiated back from the surface of the Earth into space in the form of long wave infrared-light; the other 70% reaches the surface of the Earth. [20] According to IPCC 2012 the potential energy from the sun is almost 8000 times larger than the global primary energy demand of 2008. Or stated in another way, the energy from the sun reaching the Earth without losses is around 10 000 times the global demand, which means that about one hour of sun is the equivalent energy-supply to power the entire Earth for a whole year. [21]

Downsides with solar PV (photovoltaics) are that the solar flux is affected by clouds and peaks in the middle of the day and not covering the demand during the night. For countries near the poles the availability of solar energy is also affected by seasons, with highest supply during the summer months and lowest supply during winter months.

In order to make up for this, solar PV needs to be combined with another energy source and the power storage system needs to be big enough. Electricity from PV needs to cover its own carbon footprint as well as the storage system's carbon footprint which means that electricity is produced at a high price limiting the spread of solar power. It seems that solar power alone as of now will not generate enough power to cover the entire demand but nonetheless could be an important part of a renewable energy portfolio as the price of solar power decreases.

On one hand, expensive solar cells with high efficiency made out of rare and expensive materials such as GaAs(Gallium Arsenide) have been used on a small scale and almost exclusively made for space program

applications since they are more willing to pay more for high efficiency solar cells with a low weight. On the other hand, a wide range of cells made of cheap materials such as various kinds of thin-films combined with clever efficiency-improving solutions such as using lenses or mirrors to concentrate sunlight or split the sunlight into several bands of wavelengths, are coming together making solar power on a large scale a reality. [22][23][24]

Another interesting and creative concept that is being tested is space based solar power. Where satellite-like platforms that theoretically could be harnessing solar power day-and-night are deployed in space and beams power to Earth through wireless power transmission. [25]

To get a feel for how the money paid on the electricity bill is distributed, Sweden is given as an example. Current total price on electricity in Sweden is about 31 cents/kWh<sup>7</sup>. Of that about 12.5 cents is tax, 6 cents goes to the electrical grid connection and 12.5 cents goes to the company that generates the electricity. [26][27]

When the investment in solar-cells goes below the total electricity price it is said to have reached grid-parity. The most widely used solar cells today are polycrystalline silicon solar cells and the efficiency of these is about 20%<sup>8</sup> [28]. Countries with a lot of sun e.g. Italy have already reached grid parity and many more countries e.g. Germany, Spain and Japan that have invested in solar cells are thought to follow suit by 2020. [28][29][30]

Currently Germany is world-leading in installed PV per capita and one of China's wealthiest individuals has earned his fortune in the PV-industry [31][32].

The PV demand has exceeded the supply in Germany because the governmental support for PV (and also other renewables like for example wind-power) is better in Germany than in many other countries. Examples are the feed-in-tariffs and that there is no net-metering in Germany. [34] Electricity that is not used will be sold back directly to the distribution grid, unlike for example in Sweden where the metering usually is monitored monthly and electricity generated is sold back with 12 cents/kWh. This is a disadvantage as it costs about 31 cents/ kWh to buy electricity from the grid.

Solar power constitutes a small fraction globally (0.1% or 0.005% see fig. 1 and fig. 2 above) but is advancing as more investment has been put into solar power. What is clear is that solar power has one of the biggest potential among renewable energy but it has almost the smallest usage globally because it is still relatively expensive.

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## 1.2 Motivation

### What is nanotechnology?

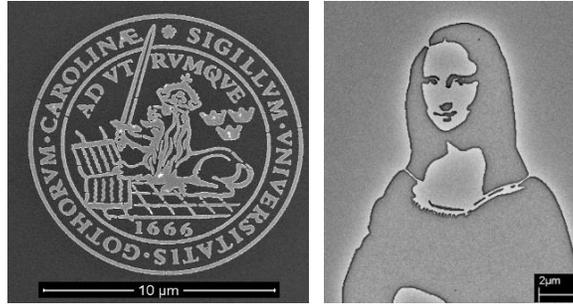
A description of nanotechnology is: *"the purposeful engineering of matter at scales less than 100 nanometers (nm) to achieve size-dependent properties and functions"* [35].

With nanotechnology, materials can be built atom by atom. This possibility has led to advances and new breakthroughs in many fields of science and technology. Below are two pictures of what can be done on this scale (see fig. 3 below). By purposeful engineering of materials, it is possible to build smaller and more powerful electronic devices(e.g. super capacitors, quantum computing chips), to enhance materials with nanostructures, making for example steel even stronger and lighter[36] and to develop bio-sensors and nanoparticles for targeted drug delivery in the medicine industry. These are all examples of the wide range of applications that nanotechnology based materials have.

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<sup>7</sup> assuming that 1USD = 6.5 SEK

<sup>8</sup> under STC (Standard Test Conditions) which means: 1000W/m<sup>2</sup> irradiance, 25°C PV-array operating temperature and AM (Air-mass) 1.5.



Examples of what can be done in very small scales.

**Fig.3(Left):** Lund university logo made with nanotechnology. The scaling bar is  $10\mu\text{m}$ . The logo has a diameter about 5 times smaller than a human hair as the diameter of a human hair is in the order of  $50\mu\text{m}$  in diameter. (Modified from Mingtang Deng).

**Fig.3(Right):** Above is a picture of Mona Lisa created by electron beam lithography, evaporation and lift-off. The scaling bar is  $2\mu\text{m}$  (Modified picture from Mingtang Deng).

### Nanotechnology combined with solar power

The combination of nanotechnology with photovoltaics is a relatively new research field. An early example of a solar cell using nano-sized structures was the Grätzel-cell<sup>9</sup> demonstrated in 1991 [37].

Silicon is a widely used semiconductor material in solar cells. About 25% of the Earth's crust consists of silicon, which makes it convenient to have as a semiconductor material in solar cells. Silicon-technology is very developed and about 85% of the solar cells today are silicon-based. [38][39]

But silicon is a material with a low absorption coefficient making it a relatively non-efficient absorber of light, demanding a thick layer of silicon-film to absorb light. Moreover the high purity requirement of silicon for well-functioning silicon-solar cells is an energy-demanding process. Therefore it might be superseded by newer technology as for example: thin-film, dye-sensitized, plastic, thermal, compound semiconductor and nanotechnology-based solar cells.

Electricity from conventional PV-modules that are based on bulk silicon is expensive compared to many other ways of generating electricity and this is where nanotechnology comes in. With nanotechnology, ways of making materials that before wasn't possible is now possible. Semiconductors made out of one-dimensional nanostructures called nanowires offer some new advantages that bulk semiconductors don't have. Producing solar cells with nanostructures such as nanowires could therefore be the important factor that finally will make solar cells cost effective.

The ideal PV-material is a strong light absorber which means that less material is needed since a thinner layer of light absorbing material can be used. Solar cells based on nanowires have this property. They can be made to be efficient light capturers with excellent anti-reflective properties while requiring less semiconductor material, and can be more efficient per surface area than bulk and thin-film solar cells. There is also not as high purity requirements on the semiconductor material as it is with conventional silicon solar cells because the light absorbing material is thinner which means that the internal losses are decreased, making nanowire solar-cells a possible cheaper and better option. [40][41][42]

Much of the work that is being done with nanowire solar cells is on the research level. In 2012 Magnus T. Borgström and his team at Lund University produced a single-junction InP nanowire solar cell with a record efficiency of 13.8 %<sup>10</sup>.

By use of multi-junction technology<sup>11</sup>, efficiencies above 30% are within reach. If nanowire solar cells reach efficiencies above 30%, it is thought that they could become commercially viable<sup>12</sup>.

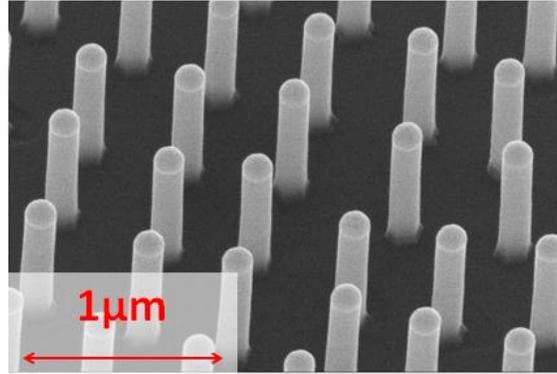
<sup>9</sup> a dye-sensitized solar cell on  $\text{TiO}_2$  films which belongs to the thin-film solar cells group.

<sup>10</sup> a  $1\text{mm}^2$  cell where the efficiency was measured by the Fraunhofer institute for Solar Energy Systems in Germany. This achievement will be published in Science in 2013.

<sup>11</sup> a solar cell consisting of many layers of semiconducting material.

Nanowire based photovoltaics will hopefully lead to efficient and low cost solar energy harvesting contributing to a sustainable development.

My thesis aims to develop, evaluate and perform photocurrent measurements on a sample called SCIL 51-84, which has III-V InP nanowire solar cells, to identify local defects in material and processing that may lead to further development of these nanowire based solar cells.



**Fig. 4:** An SEM-image with 100000 times magnification of AR28 51-82 which is a twin-sample to SCIL 51-84. This shows what SCIL 51-84 looked like with only nanowires (no front contacts) on a substrate.

### 1.3 Thesis statement and scope

Solar cells could be an important source of renewable and sustainable energy. The scope of this thesis has been to learn the necessary background information, use and further develop a photocurrent scanning technique built by Dan Hessman<sup>13</sup> and Bryan Curtin<sup>14</sup> that is capable of spatially resolving photocurrent characteristics of NW array solar cell-devices. The technique is used to resolve the photocurrent from individual NWs and allows assessing defects across the solar cell and may lead to an increased understanding of processing related defects and their impacts on PV performance. In the extension, the method has potential to enhance NW PV performance as well as significantly increase the understanding of the fundamental limitations of NW based solar cells with respect to solar energy harvesting.

During this project, scans were performed on a sample called SCIL 51-84 that had NW based solar cells on it. Furthermore, it was noticed from a previous project that a pit with seemingly no NWs contributed to a higher photocurrent than areas with NWs [43].

<sup>12</sup> according to associate professor Magnus T. Borgström at Lund University

<sup>13</sup> associate professor at Lund University

<sup>14</sup> student from University of New South Wales who did a bachelor thesis project at Lund University.

## 2. THEORY

### 2.1 PV-operation

In this section doping, pn-junction and optical properties of solar cells are described. These are all very important to discuss in order to understand the operation of a semiconductor solar cell.

#### 2.1.1 Doping

By introducing atom-impurities into an intrinsic or pure semiconductor<sup>15</sup>, one can create free electrons or holes. The electrons and holes are important for a material's conducting property and they are both carriers of electrical current.

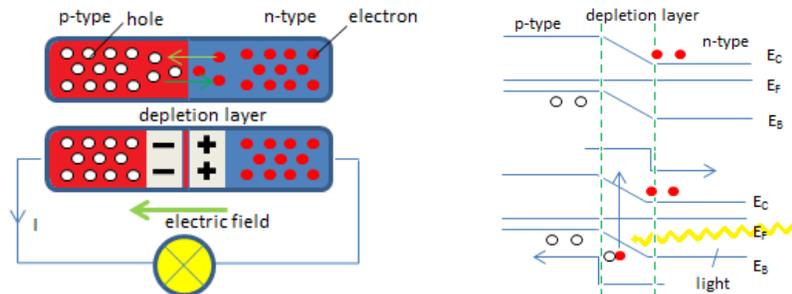
When a doped material has a majority of electrons as charge carriers, it is called an n-type material; when a doped material has a majority of holes as charge carriers; it is called a p-type material.

Silicon is a group IV material and can be p-doped with a group III material and n-doped with a group V material.

The solar cell used in this thesis were based on InP nanowires that were p-doped and n-doped with DEZn(Di-Ethyl Zinc)and TESn(Tetra-Ethyl Tin) dopant precursors respectively.

#### 2.1.2 Pn-junction

The pn-junction is present in most commercial photovoltaic solar cell devices today. A pn-junction is defined as an n-type material joined together with a p-type material. When this is done a depletion-layer is formed at the junction due to the diffusion of electrons and holes (see fig. 5(left)) that creates a built-in electric field. The bandgap energy,  $E_g$  is the difference between the conduction band,  $E_c$  and the valence band,  $E_B$ (see fig. 5(right) below) and represents the minimum energy required to excite an electron from the valence band to the conduction band and generate an electron hole pair. This means that the semiconductor is unable to absorb light with energy less than the band gap.



**Fig. 5(left):** When a p-type semiconductor is joined together with an n-type semiconductor the diffusion of electron and holes leads to an electric field in the middle over a region called depletion region. The current traveling through the circuit is denoted by  $I$ .

**Fig. 5(right):** When sunlight is absorbed in the depletion region an electron is excited to the conduction band,  $E_C$ . An electron hole pair is separated and the energy from the sunlight can be harvested and used in for example electric appliances.

When light with energy higher or at least equal to the band gap energy is absorbed in the depletion layer of the pn-junction, an electron moves from the valence band ( $E_B$ ) to the conduction band( $E_C$ ).

The photon generates an electron-hole pair that is separated spatially by the internal electric field over the pn-junction, resulting in a current that will then travel through the circuit which could be used in electrical appliances.

<sup>15</sup> pure semiconductor meaning a semiconductor without any significant amount of dopant-atoms present.

The current in the circuit is described by:

$$I = I_L - \left( I_0 \left( e^{\frac{qV}{nkT}} - 1 \right) \right) \quad (1)$$

$I_L$  = light-generated current [A]  
 $q$  = the electron charge [C]  
 $n$  = ideality factor ( $1 < n < 2$ )  
 $k$  = Boltzmanns constant [ $J \cdot K^{-1}$ ]  
 $T$  = temperature [K]  
 $I_0$  = the dark saturation current (leakage current in absence of light) [A]  
 $V$  = applied voltage [V]

This is how a solar cell using a pn-junction can generate electricity from light.

### 2.1.2 Quantum efficiency

Quantum Efficiency is the ratio between the number of electron-hole pairs created per incident photons. For a single junction solar cell the quantum efficiency alone predicts a maximum limit of 31%<sup>16</sup> for solar cells [24][44].

Quantum efficiency can be further divided into internal and external quantum efficiency.

Internal quantum efficiency counts photons that have been absorbed by the semiconductor whereas external quantum efficiency counts all photons, even those that have been reflected or absorbed by material other than the semiconductor.

When the wavelength of the incident light has an energy higher than the band gap energy of the solar cell it will be absorbed<sup>17</sup>. A material with small enough bandgap to achieve high quantum efficiency in addition to being able to absorb as much of the sun's wide spectral irradiance as possible (see fig. 6 below), will make use of most of the sunlight. For a single bandgap solar cell the optimal material is estimated to have a bandgap between 1.0 – 1.6 eV. [45] When the energy of the sunrays' wavelength is much higher than the light-absorbing material in the solar cell, much of the solar energy will be heating up the solar cell. This explains why there is a lower limit on the optimal single bandgap solar cell.

Silicon has a bandgap of 1.1eV and the nanowire solar cells used in this thesis are made of InP which has a bandgap of 1.35eV<sup>18</sup> [46]. According to Wenham 2007 this is even closer to the optimal since it is closer to 1.4 eV which in principle would absorb more of the solar-spectrum [45].

Semiconductors with many layers of semiconductors with different bandgaps are called multi-junction solar-cells. Each layer is designed with band gaps to absorb a certain range of sunlight, allowing a more efficient absorption of the solar spectra.

For a single-junction solar cell the theoretical upper limit is thought to be about 30 % [44] or 37 % (for concentrated sunlight of 1000 suns) [24] and for a multi-junction solar-cell this limit is calculated to be 72 % (for concentrated sunlight of 1000 suns, 36 junctions) [24]

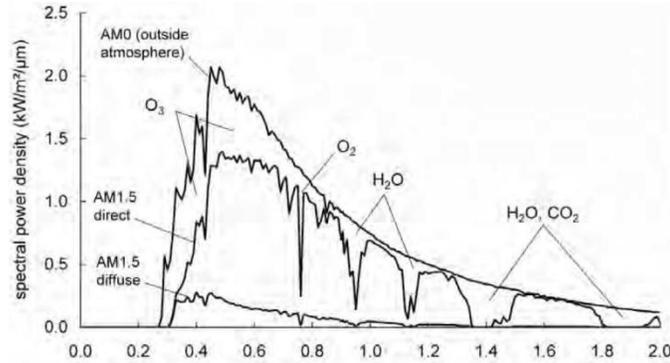
The current world record for single-junction solar cells are 25% or 27.6% (concentrated sunlight) and for multi-junction solar cells it is 37.7% or 44% (concentrated sunlight) [28]. For the solar cells mentioned above, the STC (Standard Test Conditions) are assumed which means: an air mass of 1.5<sup>19</sup>, an ideal cell temperature of 25°C (~300K).

<sup>16</sup> at a concentration of 1 sun.

<sup>17</sup> unless it is much too high, in that case it will either interact very little with the material optically, the same way high energy x-rays go through a lot of materials. Or be absorbed and release the rest of the energy as heat (thermalisation).

<sup>18</sup> in room temperature

<sup>19</sup> air in the atmosphere is an optical obstacle. AM (Air Mass) 1.5 is the average equivalent solar intensity after passing the atmosphere on Earth.



**Fig. 6:** The power density of solar flux as a function of the wavelength( $\mu\text{m}$ ) of the sunlight. AM0 is from irradiance in space and AM1.5 is the irradiance after passing the Earth's atmosphere. Visible light for the human eye ranges from about 0.39 to 0.7 $\mu\text{m}$  (from Wenham 2007).

### 2.1.3 Fundamental efficiency limits of solar cells

A major problem with solar cells is that not all light will be absorbed even though the wavelength of the light is greater than the bandgap of the semiconductor. Reflection of light on the surface is one of the reasons and happens whenever the light transitions between materials with different refractive index according to Fresnel's laws:

$$R_s = \frac{(\sin(\theta_1 - \theta_2))^2}{(\sin(\theta_1 + \theta_2))^2} \quad (2)$$

$R_s$  = Reflectance when incoming light is polarized perpendicular (*senkrecht*) to the plane

$$R_p = \frac{(\tan(\theta_1 - \theta_2))^2}{(\tan(\theta_1 + \theta_2))^2} \quad (3)$$

$R_p$  = Reflectance when incoming light is polarized parallel to the plane

$\theta_1$  is the angle of incidence and  $\theta_2$  is the angle of the transmitted beam. These two angles are calculated from Snell's law.

On a flat silicon substrate surface the reflectance is about 30 % [47]. Therefore different kinds of texturing and antireflective coatings on the surface are applied in order to decrease the reflectance [48].

In practice, solar cells also have more kinds of efficiency limitations than losses due to reflection, but in principle many of these could be completely removed [24]. Examples of such limitations are: incomplete collection of charge carriers (electron-hole pairs), absorption in non-photo generative layers and high operation temperature of the solar cell. There are also electro-technical aspects that are important, such as contact shadowing and series resistance.

If all of the extrinsic losses above could be eliminated there would remain two more intrinsic losses which are: losses caused by a single bandgap solar cell to match the entire solar spectrum and the fact that solar cells radiate some of the light they absorb (radiative recombination).

#### Nano related solar cells

Nanotechnology opens up new and potentially better ways of making materials. Solar cells built from nanostructures could deal with losses such as radiative recombination losses. [49] It is also possible to attain internal quantum efficiencies greater than 100%. Octavi et al demonstrated 130% internal quantum efficiency and 114% external quantum efficiency with multiple exciton generation on quantum dots. [50]

Most thin films have a much higher absorption coefficient than silicon. Solar cells made out of nanowires can achieve an even higher light-absorption than thin-film because there are more generated charge carriers per material in nanowires. [51] The most efficient light-absorbing nanowire structure with respect to material usage is the cylindrical shape [52].

For a period of nanowires of 610nm, core diameter of 180nm(or total diameter 260nm with the ITO(Indium Tin Oxide) and SiO<sub>2</sub>) InP nanowires and surface fill ratio<sup>20</sup> of 40%, Kailuweit et al found that less than 3% of the light( $\lambda = 470\text{nm}$ ) was reflected by the solar cell. They did not reveal the optimal fill ratio but when the fill ratio increased, the reflectance also increased. A fill ratio of 86% (nanowires and other parameters remaining the same) corresponded to approximately 7% reflectance. [53]

## 2.2 Microscopy

In the following two chapters (chapter 2.2 and 2.3), the physics behind microscopy and nanotechnology will be described.

### 2.2.1 Optical resolution limits

Light behaves like waves<sup>21</sup>. Therefore there are limits on how well a spot of light can be focused. When the hole that the light passes through is small, light with a parallel wave front will emerge as a cone due to diffraction. The result is a spot in the center with concentric circles of light, called airy discs, diminishing in intensity. When two airy discs of the first order are separable, two light dots are said to be resolved. [54]

The resolution limit of an ideal microscope is determined by the wavelength of the light source used, according to **Abbe's equation**:

$$d = \frac{0.612 \cdot \lambda}{n \cdot \sin \alpha} = \frac{0.612 \cdot \lambda}{NA} \quad (4)$$

d = diameter of laser spot [m]  
 $\lambda$  = wavelength (light source) [m]  
 $\alpha$  = half the aperture angle [rad]  
 n= refractive index between the point source and the lens  
 NA= numerical aperture

### 2.2.2 SEM (Scanning Electron Microscope)

The SEM is one of the most powerful and one of the most commonly used microscopes today. The fundamental principle of the SEM is an electron beam gun<sup>22</sup> focused into a small spot through various optical apertures<sup>23</sup>. Secondary electrons scatters back when hitting the surface of the specimen and these are detected in an electron detector, and by use of a computer, an image of the sample is created. [55]

The de Broglie wavelength of electrons can be much shorter than the wavelength of light. As Abbe's law is predicting, much lower resolutions can thus be achieved in an SEM than an optical microscope that uses light.

Using de Broglie's equation results in a slight modification of Abbe's law (4) as follows:

$$d(\text{resolution}) = \frac{7.49 \cdot 10^{-10}}{n \cdot \sin \alpha \cdot \sqrt{V}} \quad (5)$$

Knowing that the refractive index of a vacuum is 1, the aperture angle value  $\alpha$  is about 0.01radians [55] and that the amount of external voltage[V] used for accelerating the electrons in the SEM was 20kV, an estimate of about 0.5 nm serves as the ultimate<sup>24</sup> resolution limit for the SEM-pictures in this thesis.

<sup>20</sup> the ratio of the top surface of all the nanowires to the surface area of the whole substrate.

<sup>21</sup> light have both wave and particle properties.

<sup>22</sup> that can accelerate electrons with energies usually in the order of 1-40keV.

<sup>23</sup> usually two or more electromagnetic lenses operating in vacuum.

<sup>24</sup> meaning there are no losses in the optical apertures in the SEM.

In comparison, the size of a single atom is in the order of 0.1 nm in diameter.

In practice however most SEMs are not foremost limited by diffraction but more by the accelerating voltage. Too high accelerating voltages, usually over 30kV, make the electrons behave like x-rays that mostly goes through the specimen and thus limits the resolution. The resolution in a SEM also depends on the mechanical stability of the microscope and external electromagnetic interferences. [55]

The SEM used in the Lund NanoLab during this project, operates in low-noise vacuum chamber conditions and could magnify a 1\*1mm sample a maximum of about 200 000 times, showing structures a couple of nanometers long.

## 2.3 Nanowires and nanotechnology

Many of the advantages with nanowire solar cells come with the small dimensions. The direct path for charge carriers minimizes losses due to surface recombination<sup>25</sup> that is more common in most planar solar cell devices. Studies have indicated that InP nanowires are able to absorb more than 90% of the incoming light with energies higher than the band gap even at a wide incident angle of 50°, potentially saving cost and material that are normally spend on antireflective coatings. [40]

### 2.3.1 Nanowire growth

NWs can be made through various techniques and the growth processes are usually divided into two categories, a top-down approach or a bottom-up approach. The top-down approach is mostly used on semiconductor devices today and consists of carving out or cutting structures from a bulk semiconductor material. The bottom-up method consists of building up the structures atom by atom and is useful when producing structures on nanometer scale with a high crystal purity and quality. Lithography is an example of a top-down process and MOVPE (Metal Organic Vapor Phase Epitaxy) is an example of a bottom-up process.

### 2.3.2 Optical UV-lithography

Lithography is the process of making patterns on a surface by exposing light on a photosensitive material called resist. Resist is usually deposited on a semiconductor surface and a mask with holes of a certain pattern is placed on top. Then a lamp (usually UV-light) illuminates the mask and the part of the resist that is exposed to the UV-light gets soluble and is removed. The sensitivity depends on what resist that is used.

The process of high quality lithography requires an ultra-clean operating environment because a contaminant, for example a dust particle, can stick to the mask or the semiconducting surface and affect the lithography. The imbedded particle causes permanent damage to the mask resulting in lithography with more defects each time that mask is used. [56]

The cleanroom where the etching experiments were done is a class 100(ISO5) environment, which corresponds to a room that has a dust count of 100 dust-particles (0.5µm or smaller) per cubic foot or 3500 dust-particles per m<sup>3</sup>. This is said to be about 4 times cleaner than ordinary room air. [56]

### 2.3.3 MOVPE

If the substrate is made of the same material as the NWs it is called homo-epitaxy while if the substrate is different from the NWs it is called heteroepitaxy. The NW array device in this thesis was made of InP in a homo-epitaxy process via Metal Organic Vapor Phase Epitaxy (MOVPE). The most important parameters during NW growth are the partial pressures of the different precursors<sup>26</sup> in the reactor, the total flow through the reactor, the type of carrier gas and growth temperature.

The detailed chemical processes and the exact chemical reactions occurring during MOVPE are difficult to explain shortly and complex. It requires knowledge related to thermodynamics, statistics, chemistry and kinetics and is beyond the topic of this thesis. Below is a general description for the MOVPE-process used for SCIL 51-84, which consisted of 3 major steps:

<sup>25</sup> mobile charge carriers are generated and eliminated at the surface of the semiconductor.

<sup>26</sup> semiconductor material in a gaseous state.

1. Deposition of metal seed particles, (which in this case were pure Au) with a diameter as wide as the desired NW, on top of a substrate.
2. The precursors which in this case was  $\text{In}(\text{CH}_3)$ (Tri-methyl-Indium) and  $\text{PH}_3$ (Phosphine) cause growth of a InP-structure mostly below the metal seed particles. The NWs were grown in low atmospheric pressures (100mbar) at a temperature of 440 °C. Any radial growth were impeded by use of HCl(Hydrogen Chloride) which allows total control over axial and radial NW growth. [57] DEZn(Di-Ethyl Zinc) and TESn(Tetra-Ethyl Tin) were used as dopants in order to define the n and p type segments in the p-i-n InP nanowires by switching of the precursors. The i-sections of the nanowires are intrinsic sections which mean that it is not doped. [58]
3. The growth process of InP NWs is terminated by switching off the gas flow of TMI (Tri-methyl Indium), HCl(Hydrogen chloride) and the dopant precursor before cooling down to room temperature with a  $\text{PH}_3/\text{H}_2$ (Phosphine/Hydrogen) gas mixture.

### 2.3.4 Fabrication of the NW array device (SCIL 51-84)

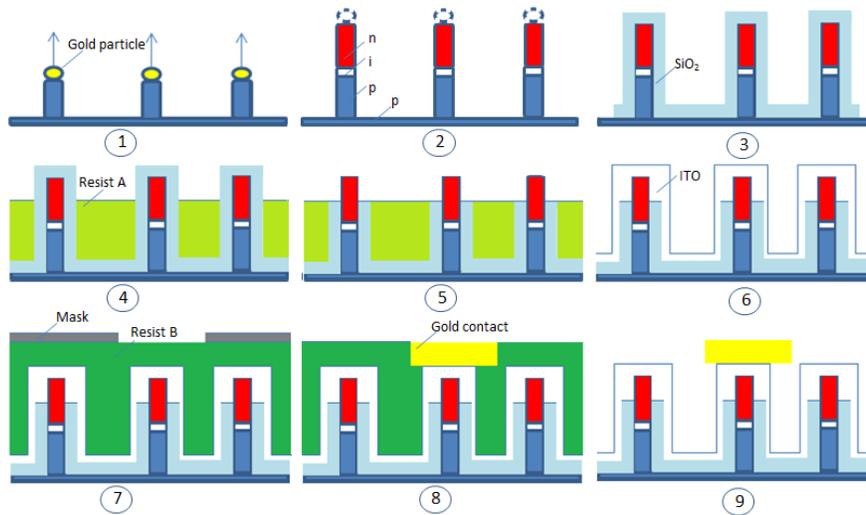
During this project, investigations and measurements were done on a sample called 51-84 SCIL, consisting of 1·1millimeter sized NW solar cells with about 4 million InP pin NWs on each cell. Each single NW had an approximate diameter of 180 nm, a length of 1200 nm and was designed with a 500 nm sized pitch between the nanowires<sup>27</sup>.

The sample was grown via MOVPE as described above and the front contact was applied using UV lithography, metal evaporation and lift-off.

The patterning of the gold-particle seeds was done by Philips in the Netherlands. Growth of the NWs was done by the Solid state physics department at LTH (Lund University) and the  $\text{SiO}_2$ , the transparent ITO contacts, and gold front contacts were defined by Solvoltaics AB in Sweden. Making the entire device consisted of a little more than 20 steps and these are described and illustrated in fig. 7 in a highly simplified and compressed manner below:

1. A p, i and n-type layer of InP nanowires are grown on a p-type InP substrate through a MOVPE process via highly ordered arrays of pure gold-seed(Au-seed) particles.
2. The gold particles are removed by use of wet chemical etching in a  $\text{KI}/\text{I}_2$ (Potassium iodide/ iodine) solution.
3. The NWs are coated with a thin layer of isolating layer of  $\text{SiO}_2$  (dielectric).
4. The array is fully coated in photoresist and etched back by use of oxygen plasma in order to expose the tips of the  $\text{SiO}_2$  embedded NWs.
5.  $\text{SiO}_2$  is removed by reactive ion etching exposing the n-type layer of the NW.
6. The resist is removed and a transparent and conducting layer of ITO was deposited, making an electric contact to the NWs.
7. A layer of the photosensitive resist is spun on top of the ITO and a mask is put on the resist.
8. The uncovered layers of resist get exposed to radiation and are removed. The mask is removed and gold (which becomes the gold-finger contact) is deposited through metal evaporation.
9. Excess Au and resist is removed in a lift off process. The NW array device is now complete.

<sup>27</sup> based on measurements from SEM-pictures on a similar sample called AR28 51-82, without ITO and  $\text{SiO}_2$  coating that had almost identical parameters as SCIL51-84.

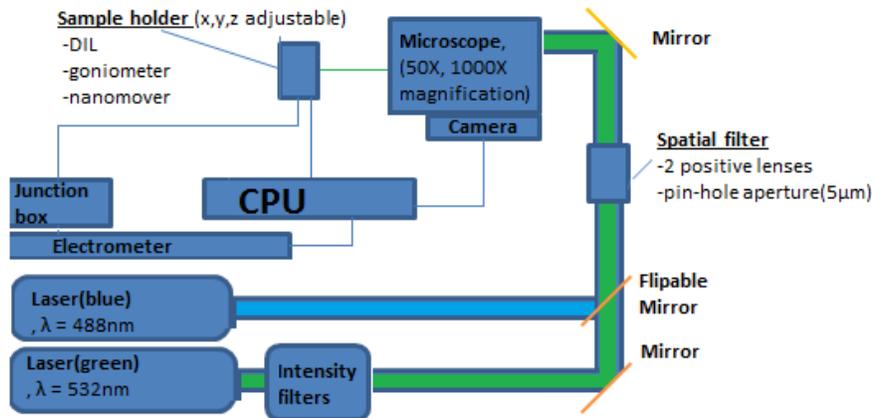


**Fig. 7:** Illustration of the fabrication steps of the nanowire solar cell, SCIL 51-84.

A caveat is that steps 3 to 9 are done by human hand and slightly different results after processing can occur even for whom lithography and etching are standard procedures.

### 3 EXPERIMENTAL WORK

#### 3.1 Design and setup



**Fig. 8:** A schematic drawing of the final experimental setup. The main parts were the laser, optical aperture, nanomover, electrometer and the computer. Raster-scans showing the photocurrent mapping of the solar cell could be performed with either a blue or a green laser.

Two lasers a solid state laser and an ion-laser, were used in the experimental setup. The green laser (was a Nd:YAG laser) with an effect of 40mW and the blue laser(was an argon-ion laser) with an adjustable output effect ranging from 0 to 60 mW.

The laser was focused through various optics into a small spot on the sample holder (see fig. 8 above). The numerical aperture value is 0.8 for the 1000 times magnification, which according to Abbe's law corresponds to a laser spot with a theoretical minimum diameter of 373nm (using blue laser) or 407nm (using green laser) during the raster-scans.

A motorized translation stage<sup>28</sup> capable of moving the sample in x, and y-axis with a minimum speed of 5000 nm/s and a maximum speed of  $6.25 \cdot 10^6$ nm/s, thus the whole solar cell could be illuminated step by step in a scanning approach and a photocurrent generated by nanowires will flow through the junction box and be registered in an electrometer. The photocurrent mapping of the scanned area is then shown on a computer. A goniometer<sup>29</sup> makes it possible to manually adjust the angle of the sample in order to orient it as perpendicular to the laser as possible.

<sup>28</sup> a nanomover called the Nanomotion II from Melles Griot

<sup>29</sup> an instrument allowing objects to be rotated to a certain angular position.

## 4 RESULTS AND ANALYSIS

### 4.1 Scans

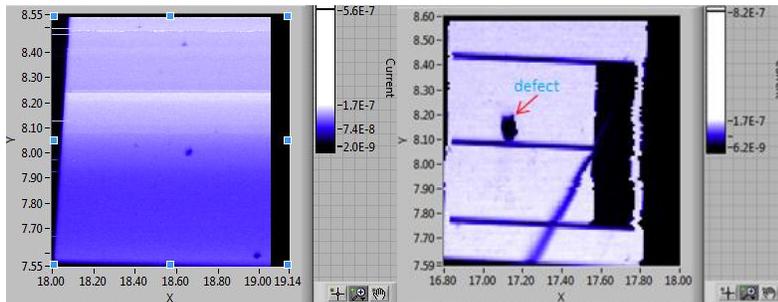
Each single solar cell was quadratic and had an area of 1mm<sup>2</sup>. Before any measurement could be done, a thin aluminum-wire was attached to the gold-contact of each solar cell by ultrasonic welding with a bonding-machine.

The SCIL 51-84 sample had 8 solar-cell devices were 7 where bonded with aluminum-wire contacts. One of the solar cells showed no significant photocurrent response during scans. Studies in the optical microscope showed that the wires were bonded on the gold-contact, making us suspect insufficient contacting in the junction-box or DIL (Dual In Line) and leaving us with 6 solar devices to measure on.

The sample is sensitive to physical damage and some scratches could be observed upon inspecting the original sample. The damages are caused by handling, for example scratches from a tweezer.

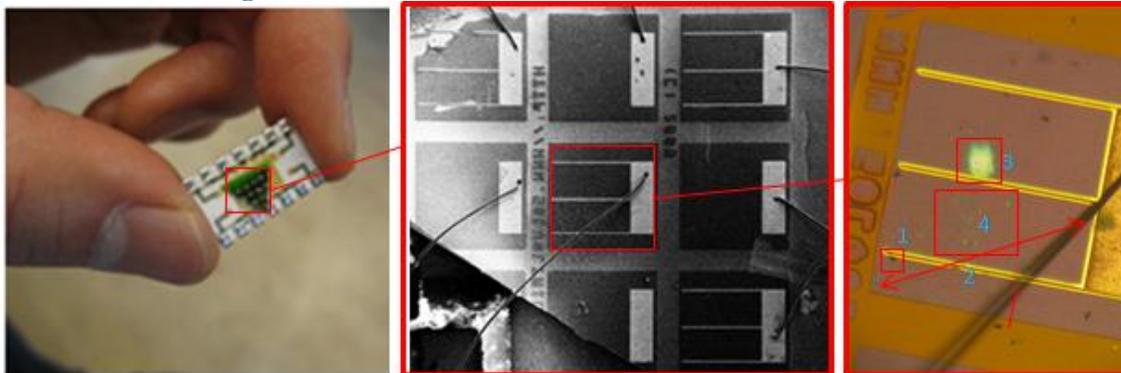
The duration of each individual scan ranged from about 5 minutes to about 3 days. The average scan took about 40minutes. A bit more than 150 successful raster-scans were saved during this project and a few of these results will be presented here.

1. A previous project<sup>30</sup> indicated higher photocurrent output from pits with seemingly no NWs. This result could not be reproduced and will be further discussed in the **Discussion** section.
2. Very long scans showed high instability. A scan that took a bit more than 70hours (see fig. 9(left) below) showed increased output of photocurrent as the time progressed.
3. One of the NW solar cells (the middle cell shown in fig. 9(right)) that I will further on refer to as NW solar cell A, showed flaws (areas with decreased photocurrent) during the raster-scans and was therefore further investigated.



**Fig. 9:** A marathon photocurrent-scan that took a bit more than 70hours and NW solar cell A with a large visible defect.

#### 4.1.1 Further investigation of NW solar cell A



**Fig. 10:** Overview photos taken of the solar cell with a camera, SEM and a optical microscope showing the 4 defect areas that was investigated. The defects were called particle (1), physical long crack (2), large green pit (3) and green blobs (4).

<sup>30</sup> Bryan Curtin's thesis from 2012 scanning with an almost identical setup as the one used in this project.

There were 4 main areas that showed decreased output of photocurrent from the NW solar cell, referred to as 1-4 in fig. 10(above). I will call each of these defects:

**Particle (1), physical long crack (2), large green pit (3) and green blobs (4).**

After studies of the SEM photos a hypothesis was formed, which was that the green colored defects were some kind of resist. This was based on the knowledge of processing steps done to fabricate SCIL 51-84 and the layer structure that could only be seen with high magnifications when tilting the sample in the SEM. To test this hypothesis, SCIL 51-84 was brought back to the cleanroom and RIE (Reactive Ion Etching) was performed with a gas of oxygen plasma on SCIL 51-84. Oxygen plasma was used because it would remove any organic contaminants without the risk of damaging the crucial ITO layer of the solar cell. Based on the morphology of the SEM pictures the most likely resist was the S1818. The expected etching rate was therefore between 0.5-2nm/s. These etching rates correspond to a total etching of 90-360nm after 3minutes etching or 240-960nm after 8minutes etching of photoresist.

Reactive ion etching was performed during 2 sessions. First, a 3 minute etching was carried out, after which an extra 5 minutes was performed. In between the steps, the sample was thoroughly studied under optical microscope. The optical microscope was used because it was the quickest option to use.<sup>31</sup> All of the 4 defects were visible in the microscope (that had 1000X magnification) either because the defects had a distinct color or because they simply were large enough but the exact change in morphology could not be seen without using SEM.

The amount of defects removed by RIE after 8 minutes of etching was practically the same as after 3 minute of etching so only the pictures after 8minutes of etching will be presented. The green blobs and the particle were affected by the RIE while the physical long crack and the large green pit showed no change after etching. This was further confirmed when studying the sample in the SEM.

Flaw number 3 was unusually large and effective in decreasing the performance of the cell. Each flaw-areas equivalent photocurrent mapping complemented with detailed SEM-photos is shown in the before-and-after etching pictures below. All of the SEM pictures below are shown with either a 0 or 30 degree tilt on the sample holder from the horizontal plane.

#### Inconsistencies in the “before-and-after” etching photocurrent-pictures

There are inconsistencies in the absolute amount of photocurrent in the before-and-after etching pictures. After 8 minutes of RIE the photocurrent output seemed to have dropped by a factor of 10. Regarding the differences in the measured photocurrents before and after processing, it cannot be used for any physical interpretation. The reason for this is that there have passed about a month of time in between those scans. In that month there have been changes and adjustments to almost all parts of the previous setup, the DIL were picked out from this setup and used in other experiments, there were re-soldering of damaged components in the DIL and junction-box and also other programmers had been adjusting or improving the software. This might have affected the amount of light illuminating the sample and also the amount of photocurrent registered in the electrometer. Therefore, focus has been put on the relative currents. Ratio differences are good measures of uniformity on the solar array and thus hopefully a good measurement of performance.

#### **1. Particle**

The particle is not completely blocking light from the laser (see fig 11 below). Studies of SCIL 51-84 under optical microscope and with different focus showed that the particle was something fluffy and relatively tall which made us suspect that it was a dust-particle. The reason we wanted to investigate this defect was because it was black like a soot-particle when studied under an optical microscope. The black color could be an indication that the area is absorbing much of the incoming light without contributing to the photocurrent.

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<sup>31</sup> the SEM requires a preparation of the sample on a special sample holder and also needs to be booked in advance since many people need to use it.

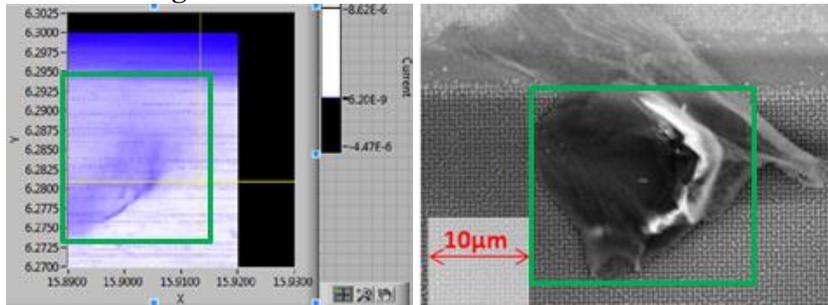
**Before etching**

Fig. 11: Photocurrent picture and SEM-picture with 6000 times magnification.

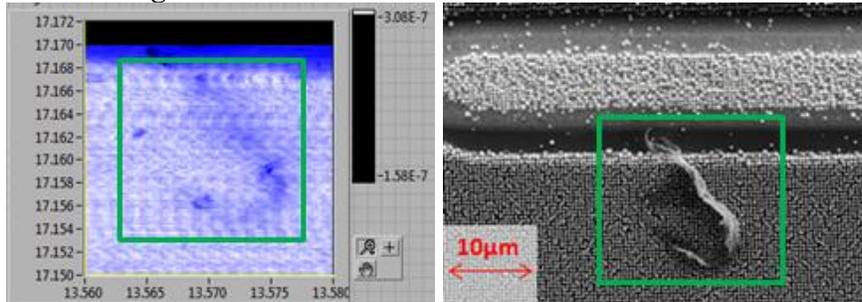
**After etching**

Fig. 12: Photocurrent picture and SEM-picture with 5000 times magnification. Much of the particle have been removed after 8minutes of RIE.

Putting the sample in the SEM (which operates under vacuum) and also used with  $30^\circ$  tilt (to the horizontal plane) did not move the dust particle even a few nanometers which means that it in some way has been attached to the solar cell. This made us suspect that the particle was a dust-particle glued on to the ITO-layer of the solar cell with resist. However the results upon inspection and photocurrent measurements after etching indicate that it was mostly resist on the top layer of the solar cell as most of the remnants of the particle and resist was gone. The resist and the covering particle on top of the nanowire solar cell corresponded to a somewhat decreased photocurrent (see fig. 11 above). The after etching picture is showing slightly more white area in the photocurrent picture (see fig. 12 above).

**Relative currents (Ampere):**

	<b>Before etching</b>	<b>Ratio</b> $\left[ \frac{High-Low}{High} \right]$	<b>After etching</b>	<b>Ratio</b> $\left[ \frac{High-Low}{High} \right]$	<b>Uniformity difference after etching</b>
<b>Low:</b>	$4 \cdot 10^{-6}$	50%	$1.7 \cdot 10^{-7}$	43%	-14%
<b>High:</b>	$8 \cdot 10^{-6}$		$3 \cdot 10^{-7}$		

The ratio decreased across the solar cell after the RIE, which is a good sign. An even better sign is that the amount of white colored pixels increased which is the equivalent of higher photocurrent area.

**2. Physical long crack**

Studies of the SEM-pictures show that the defect area has different kinds of defects. Non uniform sized nanowires, fallen nanowires, complete lack of nanowires and a pit on top of some of the nanowires. The first 3 defects seem to have arisen during the earlier stages of the manufacturing process of the gold-seed particles and possibly during NW growth. For example diffusion of the gold-seed particles on the surface, and possibly that there was a defect on the stamp which Philips used to distribute and define the gold-seeds (see section 2.3.4, fabrication step 1 and 2). Mechanical damage, for example a scratch with an extremely thin tweezer is unlikely since the crack is only about 700 nm small (in comparison, the diameter of a human hair is in the order of 50 000nm).

The pit on top of each nanowire might be caused by incomplete SiO<sub>2</sub> removal (see section 2.3.4, fabrication step 5) which has led to an uneven ITO-layer. Or it is caused by uneven etching when removing resist (see section 2.3.4, fabrication step 9)

### Before etching

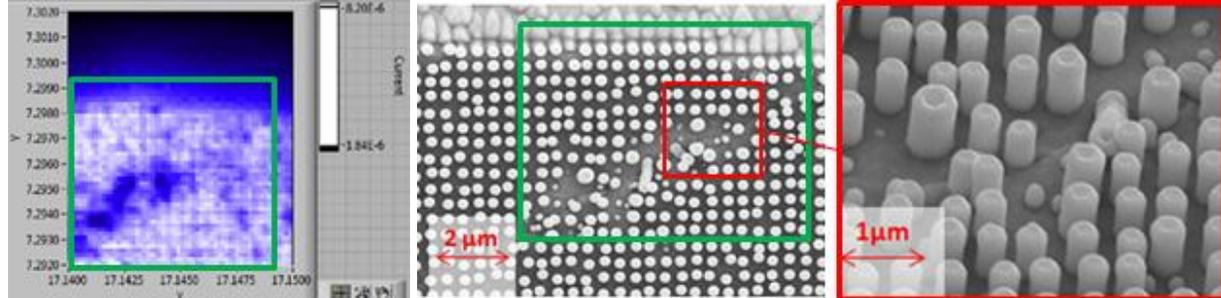


Fig. 13: Photocurrent picture and SEM-picture with 20000 and 50000 times magnification.

### After etching

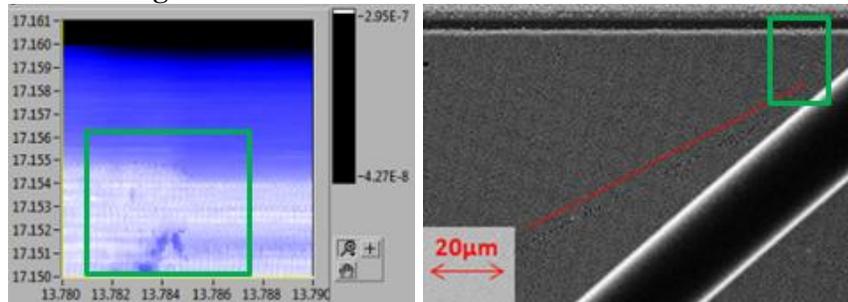


Fig. 14: Photocurrent picture and SEM-picture with 2000 times magnification. The thin aluminium-wire has moved and covers the physical long crack (parallel to the red line in the SEM-picture) near the gold-finger where the previous SEM picture before reactive ion etching was taken. This prevented zooming in on the area with 20000 and 50000 times magnification at the area shown in the *before etching* picture in fig. 13.

The SEM picture shown in the after etching has about 10 times less zoom than the “before-pictures”. This is because the aluminum-bonding wire has been moved sometime during handling of SCIL 51-84 and the area with the SEM pictures before etching is now covered. Therefore a 20000 magnification was done at the area marked with red (see fig 14) giving a visual confirmation that nothing had changed in the physical long crack and then a 2000 times magnification SEM-picture was saved to show that the defect was still there.

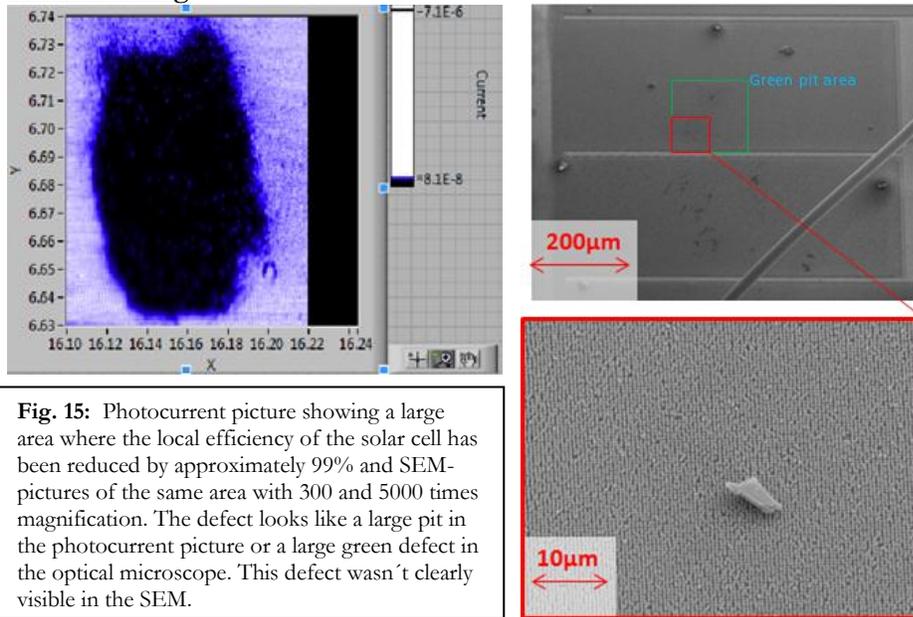
### Relative currents (Ampere):

	Before etching	Ratio $\left[\frac{High-Low}{High}\right]$	After etching	Ratio $\left[\frac{High-Low}{High}\right]$	Uniformity difference after etching
<b>Low:</b>	$1 \cdot 10^{-6}$	88%	$4.2 \cdot 10^{-8}$	86%	-2%
<b>High:</b>	$8 \cdot 10^{-6}$		$3 \cdot 10^{-7}$		

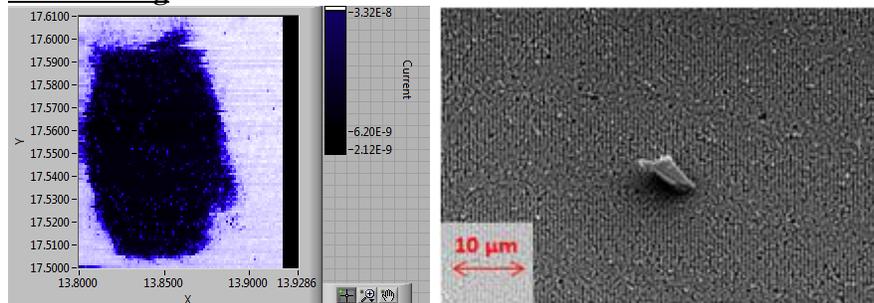
The defect large physical crack consists of defect nanowires and a ratio change of 0% was expected since the etching wasn't supposed to change the structure of the nanowires. Difference after etching was -2% which is an insignificant measured difference for this setup. We think a margin of error of  $\pm 5\%$  due to measurement inconsistencies is reasonable for this measurement setup the way it is now.

### 3. Large green pit

The reason for calling defect 3 large green pit, is because it looks like there are no nanowires in the defect area when looking at the photocurrent picture (see fig 15 below). After looking at the sample in the SEM it became clear that this isn't the case because the topography looks just like any other part of the array. There are nanowires in the defect area but they are not producing any photocurrent for some reason.

**Before etching**

**Fig. 15:** Photocurrent picture showing a large area where the local efficiency of the solar cell has been reduced by approximately 99% and SEM-pictures of the same area with 300 and 5000 times magnification. The defect looks like a large pit in the photocurrent picture or a large green defect in the optical microscope. This defect wasn't clearly visible in the SEM.

**After etching**

**Fig. 16:** Photocurrent picture and SEM-picture with 5000 times magnification. 8 minutes of RIE had no measurable or visible impact on the large green pit defect.

The large green blob was unaffected by the etching. The green pit is clearly visible in the optical microscope (the overview picture shows it as a large green spot, see fig. 10) and the photocurrent picture but not very visible in the SEM (see fig 15 above). Considering the various processing steps, the pictures from the SEM and the optical microscope imply that it is resist, that is trapped under the transparent ITO layer which is the top layer of the solar cell. This is caused by incomplete resist removal before applying the ITO-layer (see section 2.3.4, fabrication step 6)

A possible way of verifying or falsifying my hypothesis in future work would involve to etch away the ITO layer then do some RIE again. If the large green pit disappears (after studies in the optical microscope) it means that the RIE has removed the defect. If not, it means that the defect could be even deeper down, possibly under the  $\text{SiO}_2$  layer.

This experiment was not done because that would terminate any photocurrent measurements (until Solvoltaics AB have applied some new front contacts) and there was a time-limit on this project which meant that there wasn't enough time to do something like that.

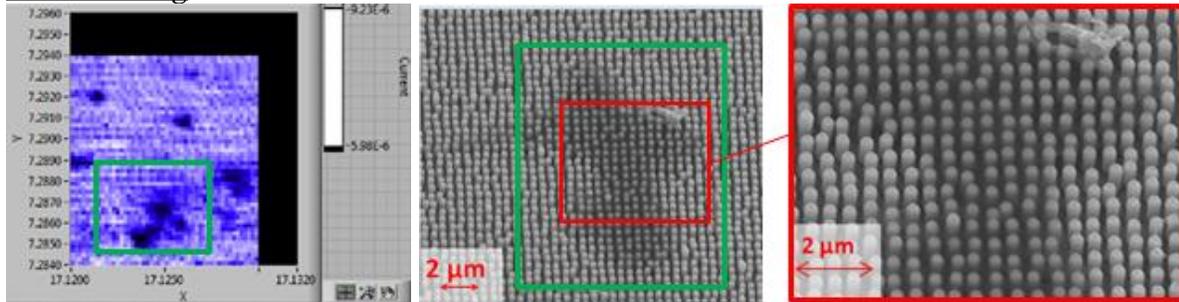
**Relative currents (Ampere):**

	<u>Before etching</u>	<u>Ratio</u> $\left[\frac{High-Low}{High}\right]$	<u>After etching</u>	<u>Ratio</u> $\left[\frac{High-Low}{High}\right]$	<u>Uniformity difference after etching</u>
<b>Low:</b>	$0.9 \cdot 10^{-7} - 3 \cdot 10^{-7}$ (in large green pit area)	98%	$2 \cdot 10^{-9} - 3 \cdot 10^{-9}$ (in large green pit area)	93%	-5%
<b>High:</b>	$7 \cdot 10^{-6}$		$3.3 \cdot 10^{-8}$		

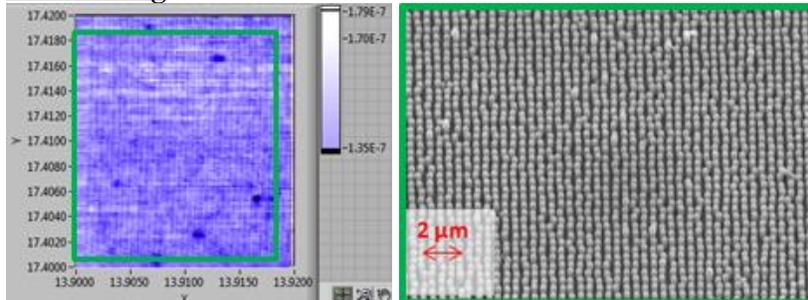
A ratio change of 0% was expected since there is no visible change in the photocurrent picture and the SEM pictures when comparing the before and after etching pictures. The result showed a 5% change in relative photocurrent which still is small enough to be due to the adjustments that had been made on the measurement setup.

**4. Green blobs**

As can be seen in fig. 17 below, the etching has successfully removed the green blobs that are thought to be resist. Our judgement is therefore that these green blobs are caused by incomplete resist removal in one of the very last fabrication steps (see section 2.3.4, fabrication step 9). Removal of the resist increased the current of the area with a calculated 40% per local area. In fig. 17(below) the resist was covering roughly 20% of a local area of a solar cell which means that a removal of the resist increased the performance locally with 8% in solar energy harvesting compared to before the etching.

**Before etching**

**Fig. 17:** Photocurrent picture and SEM-pictures with 12000 and 25000 times magnification. The two green boxes are highlighting a green blob but not necessarily the identical blob.

**After etching**

**Fig. 18:** Photocurrent picture and SEM-picture with 12000 times magnification. RIE removed much of the green blobs resulting in a more uniform solar cell performance.

**Relative currents (Ampere):**

	<u>Before etching</u>	<u>Ratio</u> $\left[ \frac{High-Low}{High} \right]$	<u>After etching</u>	<u>Ratio</u> $\left[ \frac{High-Low}{High} \right]$	<u>Difference after etching</u>
<u>Low:</u>	$5.5 \cdot 10^{-6}$	40%	$1.35 \cdot 10^{-7}$	25%	-38%
<u>Hig h:</u>	$9.2 \cdot 10^{-6}$		$1.79 \cdot 10^{-7}$		

The ratio has decreased with 38% indicating a more uniform photocurrent, after etching away many of the green colored defects. The lower values after etching (around 135nA) are represented by dark colored pixels and are very few, meaning that the overall result seems to be an improvement of the performance of the solar array.

## 5 DISCUSSION AND CONCLUSION

### 5.1 Discussion

#### 5.1.1 Defects

One thing that seems clear is that the high precision and purity requirement for producing nanowires with MOVPE up to a standard required for solar-cell industry are already existent. However the deposition processes of the dielectric ( $\text{SiO}_2$ ), transparent conducting contacts (ITO) and the gold-finger contact show some residues and contaminations for this sample.

These could be removed by further developing and improving the processing. Resist was a big contaminant for the NW solar cells that were evaluated which make it necessary to improve the steps in removal of the resist and rinsing especially before deposition of the ITO.

The spread of gold seed particles on the substrate seem to have been evenly distributed in a highly controlled manner, even though there was a severe defect (called long physical crack).

In the defect area called long physical crack, there were 3 major kinds of defects: Non uniform sized nanowires, fallen nanowires, complete lack of nanowires and a pit on top of some of the nanowires. The possible cause for these is thought to be:

- 1.) Something that went wrong during the growth of the nanowires.
- 2.) Diffusion of gold-seed particles on the substrate-surface during temperature annealing which is used in order to remove any surface oxides from the substrate before growth.
- 3.) An uneven spread of the gold-seeds from the seed particle definition. That is caused by a defect on the stamp that Philips made to distribute the gold-seeds.

The error is most likely not caused by the first reason which is growth of the NWs, since it would not be physically reasonable for the NW growth parameters to vary so strongly and so much locally.

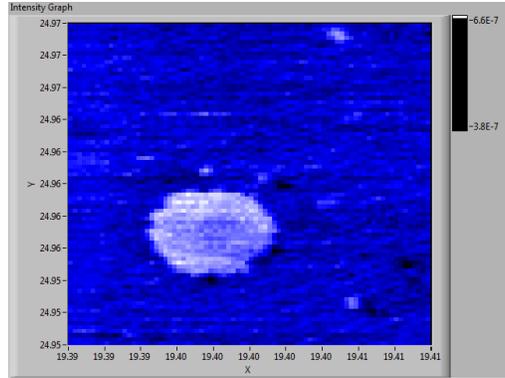
An uneven spread of Au-seed particles could have been caused by a defect on the stamp that Philips made to distribute the gold-seeds. This uneven spread of the gold-seed particles might be corrected by checking the machine that makes the stamp.

The defects called particle and green blobs were identified to be resist on the solar cell. When these were removed the solar cell became more uniform and increased in performance with about 40% compared to before etching. The reason resist decreased the performance of the solar cell is thought to be that it is an optical obstacle on the solar cell and also because it makes the surface of the solar cell more planar, somewhat removing the optical benefits of nanowires.

It is not 100% clear what and where the defect in the large green pit is. A hypothesis is that the defect is under the ITO layer and possibly even under the  $\text{SiO}_2$  layer. This could be tested by etching away the ITO layer and then perform another RIE with oxygen-plasma. If the large green pit is removed it would confirm the hypothesis that it is resist under the ITO layer of the solar cell.

#### 5.1.2 Curtin's unusual results

Dan Hessman and Bryan Curtin built much of the measurement setup in a project before mine [44]. During scans, Curtin discovered areas that looked like there were no nanowires, produced more photocurrent (see fig. 19 below).

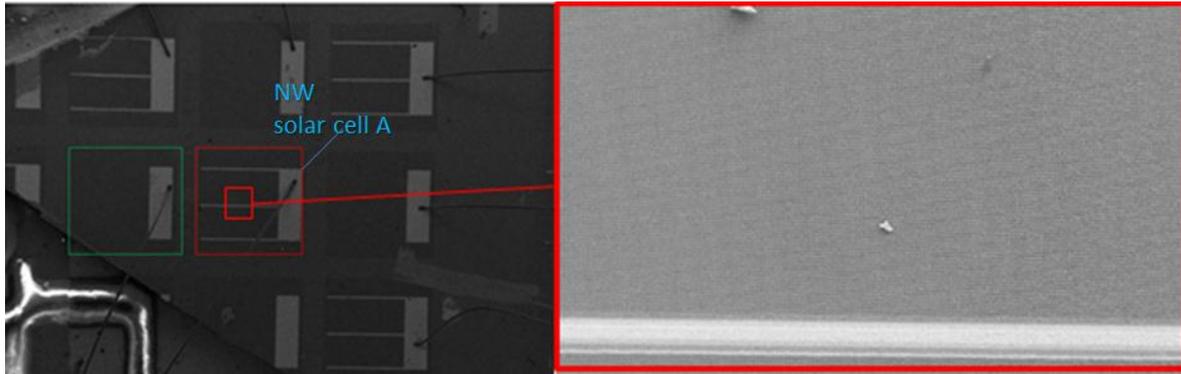


**Fig. 19:** What seemed to be a pit with seemingly no NWs produced more photocurrent than other areas on the solar cell (Curtin 2012).

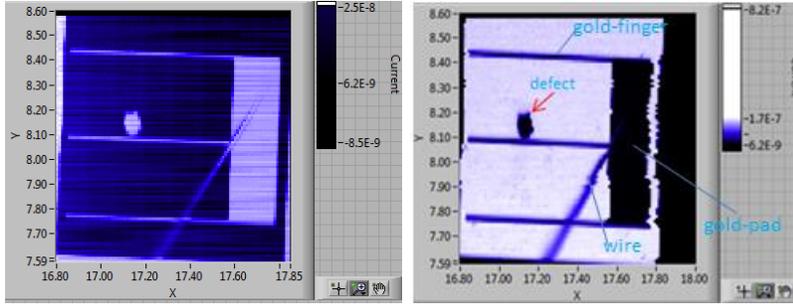
I couldn't fathom this interesting but unexpected discovery and a little more than 6 weeks were spent redoing scans, reading other papers about nanowires optical properties and learning about the experimental setup. What I was looking for in particular, was increased current in unexpected places and managed to do so in the beginning but quickly realized that these in my own experiments were due to faulty measurements that are called *inverted images*. Inverted images show higher photocurrent at unexpected areas with no exposed NWs such as gold-finger and gold-pad areas. These inverted images could explain the increased photocurrents in areas with seemingly no NWs.

#### Inverted images

The inverted images are caused by connecting the wrong solar cell to the junction box while doing a scan on another area. In this example case, the cell directly to the left of NW solar cell A was used as the contact in the junction box. The raster-scan was then performed on solar cell A and the reflection of light from it is picked up by adjacent solar cells, resulting in an inverted image (see fig. 20 and fig. 21(left) below and appendix A).



**Fig. 20:** SEM pictures with about 50 and 900 times magnification. The abnormality in the defect area that is clearly visible in optical microscopy and photocurrent measurements was not visible in the SEM. The solar cell in the green box was sensitive enough to be able to pick up reflected light from solar cell A to its right, resulting in an inverted photocurrent picture.



**Fig. 21(left):** Wrong choice of contact in the junction box resulted in an inverted photocurrent image of *solar cell A*. Inverted images are all characterized by more photocurrent in areas with no NWs. In this case the solar cell to the left of the solar cell that measurements were performed on was connected in the junction box.

**Fig. 21(right):** A correct photocurrent picture of *solar cell A*, showing different details such as a large defect, contact-wire, gold-pad and 3 gold fingers.

That the gold contacts and the Al-wire is causing increased or at least a different amount of reflection was expected because they have a different topography than the areas with nanowires. But that the large defect (see fig 21(right)) is visible with the inverted image technique was unexpected, since it is not clearly visible in the SEM that the area has a different surface height or pattern even after trying magnifications ranging from 50 to 5000 times magnification.

A way of confirming what the photocurrent mapping is able to spot would be using AFM (Atomic Force Microscopy). In simple terms it is a microscope that scans the topography of a surface by touching it with a very small needle. This method was not used because confirming the exact topography wasn't prioritized and because using this method involved a risk of permanently damaging SCIL51-84 with scratches. I think it could be interesting to perform an AFM on SCIL 51-84. What is expected is a large group of slightly higher or lower nanowires in the area called defect. An hypothesis is that the defect area is probably higher by just a few nanometers, since that would be congruent with both that there's a layer of something (most likely resist) under the ITO (making that area slightly higher) and the inverted image in fig. 21(left).

The result Bryan Curtin observed with more photocurrent in areas with seemingly no NWs could not be reproduced with SCIL 51-84. However, I think it is too early to reject what Bryan observed. For example V.E. Ferry et al that in 2011 have done several different light trapping experiments with nanostructures states that the spatial correlations and topography of random or periodic arrangements of the light-scattering nanostructures is still unclear.[60] Moreover the n-segment of the NWs on Bryan's sample was longer than the NWs on the sample I was measuring on (SCIL 51-84) meaning that the physical and optical properties of for example the NWs could be very different.

A way of determining what Bryan observed is to redo raster-scans on the sample he had but unfortunately that wasn't possible because that sample was in Australia during the time-span of this project.

### 5.1.3 Evaluation of measurement-setup

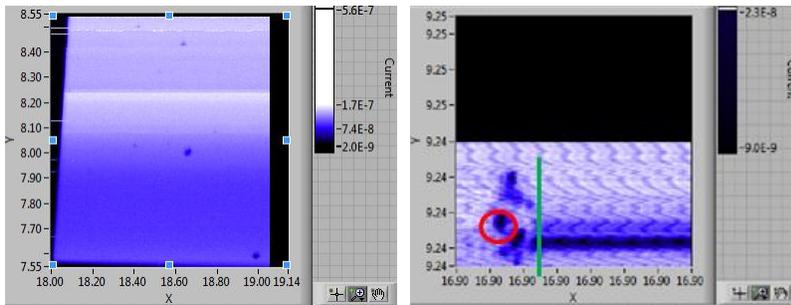
The minimal step size 10nm and the minimum speed of 5000 nm/s for the motorized translation stage (nanomover) together with the diffraction limited laser spot size serves as the major limits on how small the pixel size of the raster scans can be.

As the pixel sizes decreased the scan time also became longer. A way of counteracting this is to scan smaller and smaller areas. A downside with this is that this method only seems to work efficiently on defect areas and that I found it easy to get lost<sup>32</sup> in what area that was scanned when the scanned area is less than a micrometer. There are also motor-torque and turning-screw errors from the nanomover.

<sup>32</sup> many areas on the solar cell had a very uniform spread of NWs. But a uniform scan could as well be a uniform background noise from ambient light.

There is a maximum of 150nm positional error and the Nano motion II nanomover guarantees a bidirectional repeatability of  $\pm 100\text{nm}$ . This is why the scanned area shouldn't get too small. If the scanned area is big enough to include a known characteristic feature such as an unusual defect or gold-finger then there will be less guessing in what area that was scanned. Any systematic errors from the nanomover that always exist would therefore be negligible.

A long scan that was supposed to scan an area of  $1\cdot 1\text{mm}$  took a little more than 70 hours to perform. The pixel size was about 700nm. The marathon-scan shows much less background noise than usually which is good. But the experiment also shows two kinds of flaws with the setup. One is that the intensity increases with time and the other is that the entire area of the cell is not shown in the photocurrent picture (no signs of gold-fingers, gold pad or aluminum-wire) (see fig. 22 below).



**Fig. 22(left):** A marathon-scan that took a little bit more than 70hours showing instability from the laser that is more visible during longer scans.

**Fig. 22 (right):** The defect (a green blob) marked with a red circle is only about 800nm in diameter. The measurement was unsuccessful to the right of the green line as it looks like the measurement setup has crashed.

Later another experiment was performed with a scan over a  $10\cdot 10\mu\text{m}$  and a pixel size of 70nm. Both fig. 22 (left) and fig. 22 (right) above shows the same problem, which is that the photocurrent picture crashes in x-axis when the limit of the setup is pushed. That limit is usually during scans with a pixel size smaller than 700nm. The nanomover was moving and the electrometer were registering photocurrents during the scans so something with the computer or the programme code might be causing these crashes.

The different intensity from the marathon scan could be caused by for example that the laser isn't intensity stabilized or that different amount of light gets through the pin-hole aperture at the spatial filter area. Both problems could be reduced by normalizing by normalizing the current over time in the software or by putting up detectors detecting scattered laser light near the spatial filter area and compensating for intensity changes or by a system involving for instance an Acousto-Optic Modulator<sup>33</sup>.

## 5.2 Conclusions and future outlook

A mistake from my side resulted in something called the inverted image. This technique is a potentially quicker way and also smaller risk of physically damaging NW solar cells than AFM when determining topography abnormalities on the NW solar cell sample. The question is with what precision? That requires a careful AFM profiling, especially on the defect area called *large green pit*.

An important result was that 8 minutes of RIE with oxygen plasma could remove resist on the solar cell. This improved the efficiency of the solar cell. Resist that probably is under the ITO or the  $\text{SiO}_2$  layer of the solar cell was not removed with this technique.

<sup>33</sup> a recommendation from Andreas Walther from the atomic physics department at Lund University.

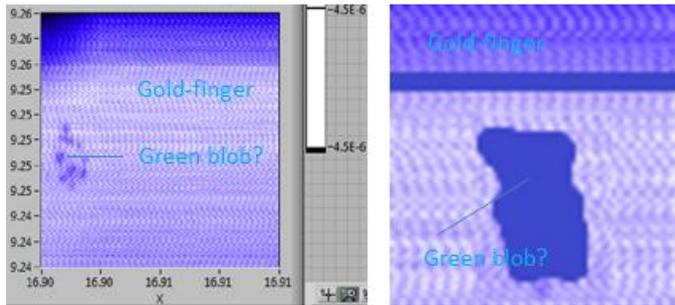
### Lessons learned

A mistake I did was adjusting the setup in between the “before-and-after” pictures. If I redid this project there would be a limit of 8 weeks to get familiar with and make improvements and adjustments to the entire setup. After that period there should not be any big changes, to get consistent photocurrent pictures. Doing the photocurrent scans is repetitive work which makes it extra important to keep logs on each scan. I had an entire binder full with logs from these scans and a draft of the logs to the scans is in appendix B. When doing scans with 1000 times magnification there will be a slight improvement on the resolution by manually adjusting the focus on the microscope with time as the scan progresses.

Limits on this measurement setup are:

**-The optical resolution:** a blue laser was installed to decrease the spot size of the laser. This is about as far you can go with optical spectroscopy due to diffraction.

**-The nanomover:** I believe that the nanomover haven't reached its limit yet as it can move with a step size of as low as 10nm and could therefore possibly handle pixel sizes around 100nm. The disadvantage is the slow scanning speeds when the pixel size gets small, in particular smaller than 700nm. Scanning over a small area of  $10\mu\text{m}\cdot 20\mu\text{m}$  with a pixel size of 50(x-axis) and 100nm (y-axis) took about 30minutes but more importantly the result wasn't as good as hoped (see fig.23 below).



**Fig.23:** The left picture is a photocurrent scan with a pixel size of  $50\cdot 100\text{nm}$ . The gold finger contact is crooked and the green blob is much smaller than expected. The expected photocurrent picture is illustrated on the right.

Since I didn't notice any abnormalities with the electrometer or the nanomover during scans with crashes I am suspecting that the error lies in the lab-view programming code together with the instable laser.

### Suggested improvements and future experiments

**-The area that could be scanned:** The nanomover can move a maximum of 2.54cm in the x-and y-axis. In the future, larger arrays of NW solar cells might be produced. Considering a nanomover that could move longer distances, ideally a bit more than  $10\text{cm}^2$  could be a small improvement to the setup.

**-Taking more advantage of colors:** The small area scan performed in fig 22(right) would have had 10 000 pixels, each representing a photocurrent. The marathon-scan in fig. 22(left) has about 600 000 pixel points<sup>35</sup>. That amount of data is not something you want to look through manually pixel by pixel. There is so much photocurrent information that could be clearly and quickly presented with colors directly during scans instead of monitoring the setup during the scan or going into the programme manually using a cursor. A suggestion is the way the photocurrent picture looks below in fig. 24 where they have used most of the color spectrum.

<sup>34</sup> because most standard single-crystal solar cells today have an area of about  $10\text{cm}\cdot 10\text{cm}$

<sup>35</sup> and almost 2 million pixel points if the scan didn't crash.

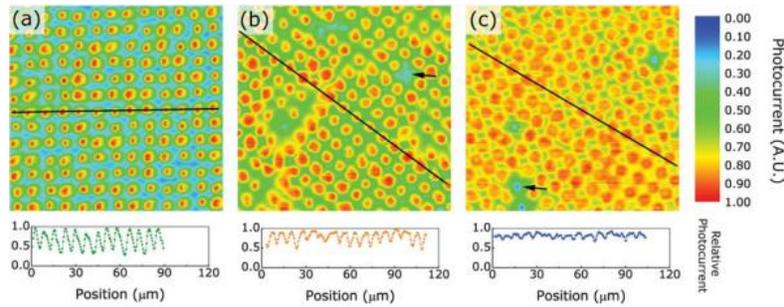


Fig. 24: Silicon nanowire arrays presented with a large range of the color spectrum (Putnam 2010).

Many of the defects have a distinct color that quickly can be detected with a 50 time magnification with enough bright-field on the microscope and think that one should consider buying a camera showing colors that can be mounted on the microscope. The grayscale camera that is used now could be kept as an alternative camera in the setup because it is good at showing contrasts at uniform areas with no distinct color differences.

**-The time variance:** the variance of the laser is definitely something that should be looked into and one of the more important things that need to be dealt with. When scanning areas with low speeds the time variance error takes over.

This time variance could be tested by measuring the intensity of the laser over a long time, i.e. 70 hours and see if it is increasing over time like the marathon-photocurrent scan is showing.

If this is not the case, then we suspect the spatial filter. This could possibly be tested by installing two detectors measuring the laser intensity over time. One of the detectors is placed before and the other is placed behind the spatial filter because it is suspected that the amount of light passing through the pin-hole aperture could be the source of the time variance with the laser intensity.

**-Connection resistance:** If NW solar cells will be put into commercial use, it is likely that the NW solar cells will be connected into a module the way today's commercial solar panels are. Doing raster-scans on NW solar cells that are connected with a gold-finger or an aluminum bonding wire is a way of finding out more about how NW solar cells behave.

The only home we have which is planet Earth is in trouble. Rapid climate change and large environmental pollution effects are going to have a severe negative effect on humans if we keep our society based on burning fossil fuels.

Some people claim that we already have passed the point of no return. That the tipping point of global warming has already passed for example.

I believe that we should focus on asking ourselves *what if* questions. Focusing on what can be done. Keep educating ourselves and teaching others after best ability. Keep giving support to technologies, political and economic frameworks that are aiming to be sustainable or maybe even consider populating other planets. But the horizon and potential for solar energy is looking bright, making me cautiously optimistic about the future of nanowire solar cells as part of a sustainable and long-term solution.

## ACKNOWLEDGEMENTS

Even though there is only one author to this thesis much of the work was done in cooperation with others. I would therefore like to give credit and thanks to:

Dan Hessman for showing and teaching me how to use the equipment in the optics laboratory.

Magnus T. Borgström for teaching me about nanotechnology, for guidance and continuous feedback on my work.

Thanks to Vishal Jain, one of the many good people I have encountered in the solid state physics department at Lund University, which I enjoyed working and cooperated with the most in the nanolab cleanrooms and with the SEM.

Thanks to my very trusted proof readers Donald Morrow and Karl Kan.

I would also like to give my blessings and gratitude to everyone that in any way has contributed to this thesis.

## Appendix A Inverted images

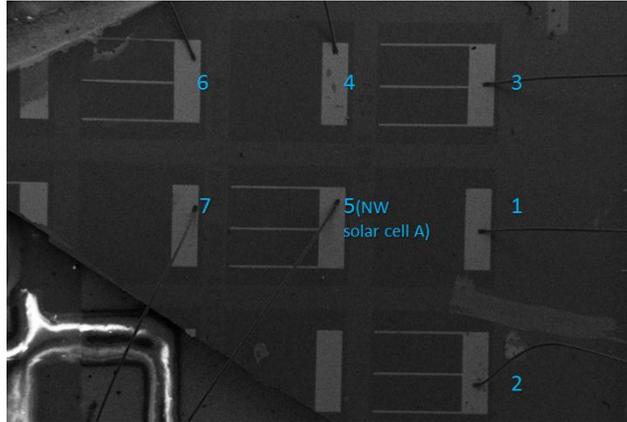


Fig. 25: An overview picture of SCIL 51-84. Each solar cell is named with a number from 1 to 7.

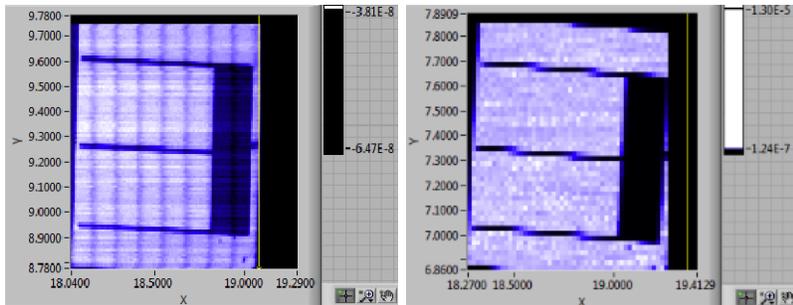


Fig. 26: A good quality inverted image of solar cell 3 caused by light picked up by solar cell 1 beneath it. The correct image is on the right.

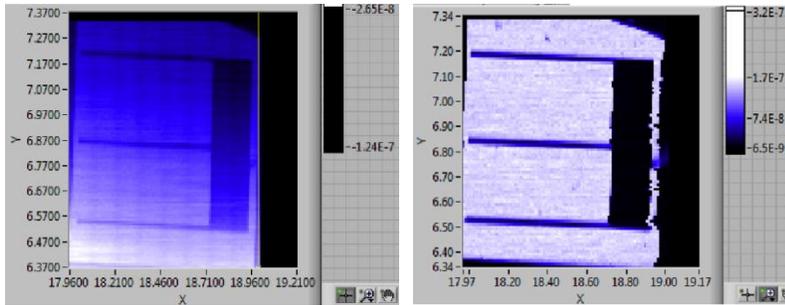


Fig. 27: A bad quality inverted image of solar cell 2 caused by light picked up by solar cell 3, located 2 solar cells or approximately 2mm above it. The correct image is on the right.

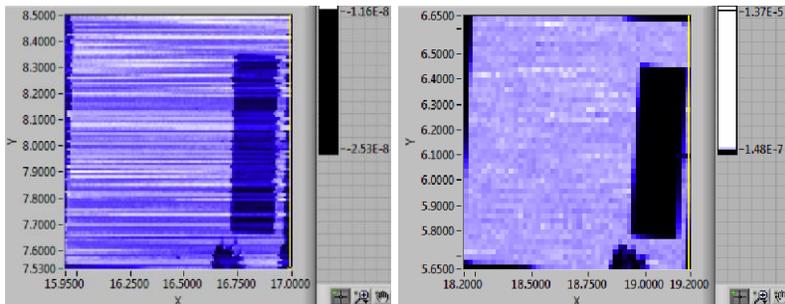


Fig. 28: A bad quality inverted image of solar cell 1 caused by light picked up by solar cell 2, located beneath it. The correct image is on the right. Based on studying the results of fig.25 to 28, the inverted image technique gives a better inverted image connecting solar cells with just a gold-pad compared to connecting solar cells with gold-pad and gold-fingers.

## Appendix B

### Raster-scan log

DATE:	MEASUREMENT NBR: (Name/descr.)	SAMPLE NBR: CONTACT: BF(Bright Field):
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#### SETTINGS:

##### INTENSITY FILTER:

MICROSCOPE	10· 5X ; 10· 100X
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<b>NANOMOVER</b>		
START:		
END:		
Dwell time:		
x# steps		
y# steps		
Speed:		

(place for sketching the NW solar cell)

<b>ELECTROMETER</b>	
RATE	FAST; MEDIUM; SLOW
NEGATE	ON; OFF
AUTO	ON; OFF

<b>RESULT</b>		
TOTAL SCANNINGTIME:		
PHOTOCURRENT		
PIXELSIZE:		
COMMENT:		

## Appendix C

### Solar Cells on the Ecology Building in Lund

Annual electricity generation: 79 MWh

The total cost for the installation was 7,2 MSEK (including design). Akademiska hus received 70% in investment subsidy. In 2012 the maximum subsidies would have been 45%.

a) Simulate the expected output for the PV-system with the program Winsun0709. Calculate for 1kWp for each installation and multiply. Then fill out the table below.

Modules	Area modules A [m <sup>2</sup> ]	Installed Power P [kWp]	Efficiency $\eta = P/A$	Annual irradiation [kWh/m <sup>2</sup> ]	Annual electricity generation [MWh/y]
Facades 90°	192	23.9	0.13	773	16,4
Sunshade 40°	54	5.97	0.13	1119	6,13
Roof 0°	523	79.1	0.15	977	67,5
<b>Total</b>					<b>90,3</b>

b) The monitored output from the system for 2009, 2010 and 2011 on the webpage of the Ecology Building is checked:

[http://195.198.213.14/\\_d2f4867c1229f385895de4f6f7fa1564\\_/?s=main](http://195.198.213.14/_d2f4867c1229f385895de4f6f7fa1564_/?s=main) (2013-01-26)

Monitored output	2009	2010	2011
Electricity Generation MWh/year	78,7	72,9	76,9

The simulated results are approximately 14 % higher than the monitored output. This can be due to following:

- Simulations are simulated under standard test conditions, STC (25°C), while real conditions differ from this standard value, causing efficiency losses.
- Clouds and shading (dirt, snow, etc.) cause lower performance.
- According to *Utvärdering av solsystem* more than 4 % losses are from the inverters.
- According to *Utvärdering av solsystem* 3-5 % losses are due to drying and cooling the equipment room.

c) A new calculation with the program on the link below was made:

<http://re.jrc.ec.europa.eu/pvgis/apps4/pvest.php>

The previous results with the results from this program are compared and the results are discussed.

Modules	Area modules A [m <sup>2</sup> ]	Efficiency $\eta = P/A$	Annual irradiation [kWh/m <sup>2</sup> ]	Annual electricity generation [MWh/y]
Facades 90°	192	0.13	809	$0,628 \cdot 192 \cdot 0,13 = 15,7$
Sunshade 40°	54	0.13	1130	$0,876 \cdot 54 \cdot 0,13 = 6,2$
Roof 0°	523	0.15	971	$0,73 \cdot 523 \cdot 0,15 = 57,7$
<b>Total</b>				<b>79,6</b>

There is agreement between measured performance and simulations from jrc.ec. The results from jrc.ec are therefore much more realistic compared to the results from the simulation programme Winsun. This means that the website jrc.com probably has better measurements and weather statistics of the real irradiance.

d) Calculation of the total investment per annually delivered kWh.

The yearly production,  $p_{\text{mean}} = (76\ 200 \text{ kWh/year})$  is a calculated mean value from Ecology Building's electricity-generation during the last three years (2009-2011).

$$C_{el}(\text{electricity cost}) = \frac{G(\text{Initial investment})}{p(\text{produced electricity}) \cdot l(\text{technological lifetime})} = \frac{\left[ \frac{\text{SEK}}{\text{years}} \right]}{\left[ \frac{\text{kWh}}{\text{year}} \right] \cdot [\text{years}]} = \frac{[\text{SEK}]}{\left[ \frac{\text{kWh}}{\text{year}} \right]}$$

$G = 7,2 \cdot 10^6$  SEK,  $p_{\text{mean}} = 76200$  kWh/year,  $l = 25$  years (own estimation)

$C_{el} = 3,8$  kr/(kWh\*year) = **380 öre / (kWh\*year)**

*e) Calculation of the capital cost per delivered kWh with the annual installment method. Use the annuity factor for 25 years depreciation period and discuss the results.*

$a_1$  the real interest rate of 4% ( $a(\text{annuity}) = 0.064$ )

$a_2$  as well as 7% ( $a = 0.085$ ).

$$C_c(\text{Capital Cost}) = \frac{G(\text{initial investment}) \cdot a(\text{annuity factor})}{p(\text{produced electricity})} = \frac{[\text{SEK}] \cdot \left[ \frac{1}{\text{year}} \right]}{\left[ \frac{\text{kWh}}{\text{year}} \right]} = \frac{\text{SEK}}{\text{kWh}}$$

### 1) for the total cost

$G_1 = 7,2 \cdot 10^6$  SEK,  $p_{\text{mean}} = 76200$  kWh/year

$a_1 = 0,064$  (4% on 25 years) →

$C_c(\text{Total})_1 = 6$  kr/kWh = **600 öre/kWh**

$a_2 = 0,085$  (7% on 25 years) →

$C_c(\text{Total})_2 = 8$  kr/kWh = **800 öre/kWh**

### 2) for Akademiska hus (the owner) that got 70% subsidy from the Swedish government.

$G_2 = 7,2 \cdot 10^6 \cdot 30\%$  SEK =  $2,16 \cdot 10^6$  SEK,  $p_{\text{mean}} = 76200$  kWh/year

$a_1 = 0,064$  (4% on 25 years) →

$C_c(\text{for Akademiska hus})_1 = 1,8$  kr/kWh = **180 öre/kWh**

$a_2 = 0,085$  (7% on 25 years) →

$C_c(\text{for Akademiska hus})_2 = 2,4$  kr/kWh = **240 öre/kWh**

### 3) the energy cost with the subsidy today(45%)

$G_3 = 7,2 \cdot 10^6 \cdot 55\%$  SEK =  $3,96 \cdot 10^6$  SEK,  $p_{\text{mean}} = 76200$  kWh/year

$a_1 = 0,064$  (4% on 25 years) →

$C_c(\text{PV system investment in Sweden year 2012})_1 = 3,3$  kr/kWh = 330 öre/kWh

$a_2 = 0,085$  (7% on 25 years) →

$C_c(\text{PV system investment in Sweden year 2012})_2 = 4,4$  kr/kWh = **440 öre/kWh**

440 öre/kWh is most likely an overestimation because the investment cost for the same amount of PV cells today (year 2012) is probably much lower than 7.2 MSEK.

As the prices for PV-cells has decreased during the last years one more calculation will be made, estimating today's investment cost for the same amount of PV modules. Assuming that the subsidies and the cost are lowered in approximately the same proportion to each other, the cost is estimated to be 3.5 MSEK today.

### \*4) Investing in a large PV-system under current(year 2012) conditions with subsidy(45%).

$G_4 = 3,5 \cdot 10^6 \cdot 55\%$  SEK =  $1,925 \cdot 10^6$  SEK,  $p_{\text{mean}} = 76200$  kWh/year

$a_1 = 0,064$  (4% on 25 years) →

$C_c(\text{more realistic PV system investment in Sweden year 2012})_1 = 1,6$  kr/kWh = **160 öre/kWh**

$a_2 = 0,085$  (7% on 25 years) →

$C_c(\text{more realistic PV system investment in Sweden year 2012})_2 = 2,1$  kr/kWh = **210 öre/kWh**

**Discussion and comments:**

The investment for Akademiska Hus was not only made with the purpose to save energy, but also to make an example and increase the knowledge and science of PV-cell plants. Although there is a decrease of the production cost during recent years, subsidies are needed because the PV-modules are still relatively expensive and simply not cost effective.

Electricity in Sweden in 2012 costs about 1.2 SEK/kWh. Of that  $\approx 0.5$  SEK is tax,  $\approx 0.2$  SEK goes to the electrical grid connection and  $\approx 0.5$  SEK goes to the company that generates the electricity. This means that when the kWh cost goes below approximately 1,2 SEK the PV-modules will start to save both electricity **and** money, considering current market price on electricity.

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## FIGURES

**Fig.1:** IPCC 2012, Renewable Energy Sources and Climate Change Mitigation, <http://srren.ipcc-wg3.de/report> , p.186, February 2013

**Fig.2:** IPCC 2012, Renewable Energy Sources and Climate Change Mitigation, <http://srren.ipcc-wg3.de/report> , p.187, February 2013

**Fig.3:** Mingtang Deng, modified picture from: <http://www.nano.lth.se/tibet/template/personal%2CIndex.vm?pageid=232957&siteid=1040>, December 2012

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**Fig.5:** Author's picture (2012)

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**Fig.10:** Photo-montage consisting of author's camera pictures and picture from Lund nano lab (2012)

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**Fig.20:** Photo-montage consisting of pictures from Lund nano lab (2012)

**Fig.21-23:** From the measurement setup used in this thesis (2012)

**Fig.24:** M. e. a. Putnam, "Si Microwire-Array Solar Cells," *Energy & Environmental Science*, vol. 3, no. 8 2010, November 2012

**Fig.25:** Lund nano lab (2012)

**Fig.26-28:** From the measurement setup used in this thesis (2012)