Main S&T results/foregrounds

Main results and foregrounds presented below follow the R&D workplan which has been devided into 6 major R&D topics: i) Nanoparticle based materials (WP1), ii) Nanowires (WP2), iii) Ultrathin nanolayers (WP3), iv) Electrical, optical and structural properties of individual nanomaterials (WP4), v) Design, processing, charaterisation and testing of solar cells and modules (WP5), and vi) Assessement of transferability to industrial production (WP6).

NANOPARTICLE BASED MATERIALS AND RELATED SOLAR CELLS

Work on this topic was part of WP1, which had the following objectives:

- To fabricate individual nanoparticles with desired optical and electrical properties, composition, purity, crystallinity, particle size etc and inks to disperse such nanoparticles in a desirable manner
- To optimise processes for incorporation/assembling of semiconductor nanoparticles in thin films, which can be used as a part of solar cell structures, providing: (i) nano-particle based emitter (ii) MEG process, (iii) up- and down conversion (shifting) effects
- To optimise processes for incorporation of metallic nanoparticles, which can provide: (i) formation of local contacts or (ii) surface plasmon based improvement of the solar cell conversion efficiency
- To develop cost-effective non-vacuum and vacuum based equipment and processes for the formation of nanoparticles embedded in different solid matrices and thin layers or assembled in nanolayers

During the project period, cost-effective processing of nanoparticles and related inks adjusted to PV needs has been developed in WP1. The developed processes have been used as a background for innovative technologies based on an implementation of nanoparticles in PV. Manufacturing procedures for the processing of nanoparticles and inks compatible with industrial requirements have been developed in WP1. Several alternative methods have been compared for cost-effective production of such nanoparticles: sol-gel, laser assisted, thermal spraying, magnetron sputtering, etc.

Synthesis of nanoparticles and inks

Several vacuum (magnetron sputtering, e-beam deposition, PECVD, H+ plasma) and non-vacuum (sol-gel, laser ablation, cryo-milling, reduction of oxides by annealing, reduction of oxides by hydrogen radicals) technologies have been developed to sinter semiconductor and metallic based nanoparticles, suitable for PV applications. Several types of inks have been successfully tested to disperse NPs and to form layers from NPs containing solutions.

Different methods of deposition of colloidal Ag NPs of 100-nm and 200-nm diameters bearing different stabilization ligands (PVP and Citrate) on different surfaces (Si, SiO_2, SiNx, ZnO) were elaborated, such as deposition by physical adsorption and adsorption due to chemical functionalization of a solar cell interface.

Developments based on implementation of vacuum methods (PECVD, e-beam) for forming arrays of Si nanoparticles in SiO_x were performed. Some indications, that such Si NPs can be formed in this way were obtained. Formation of Si NPs on top of Si has been realised in frame of room temperature process. Implementation of the developed NPs and related layers for the processing of advanced solar cell structures has been done during second period of the nanoPV project activity and results can be seen in the section on Design, processing, charaterisation and testing of solar cells and modules.

Nanoparticles for fabrication of heterojunction solar cells

Results of this type of developments can be summarized as follows:

- Heterojunction Si based solar cells have an emitter, which consists of highly conductive local regions. These conductive local regions provide current flow through the ITO/a-Si:H interface. It can be assumed that such channels can be constructed from highly conductive Si nano-particles.
- It has been shown that microcrystalline or rather nanocrystalline emitter layers processed by PECVD are compatible with high efficiency heterojunction solar cells if a nanometer-thin intrinsic amorphous buffer layer is used for interface passivation.
- Si NPs solutions based on ethanol with different concentration of Si NPs have been prepared. Thin mono-layers of such Si NPs based solutions have been successfully deposited on a-Si:H/Si solar cell structures, which shows reasonable values for the minority carriers lifetime and will be used for further processing of solar cells.
- It is shown that a-Si:H layers deposited at low temperatures on Si substrates can be converted into Si NPs containing layers after annealing at 700-800 °C.

Silicon heterojunction solar cells with aSi:H emitter layers and indium nanoparticles have been prepared by H-plasma induced reduction of an ultrathin ITO layer with a thickness of 5 to 10 nm. As substrate n-type wafers with a planar (100) surface and with an alkaline etched, random pyramids texture have been used. A conventional a-Si:H emitter stack based on ultrathin layers and additionally a 5 to 10 nm thin ITO layer has been deposited.

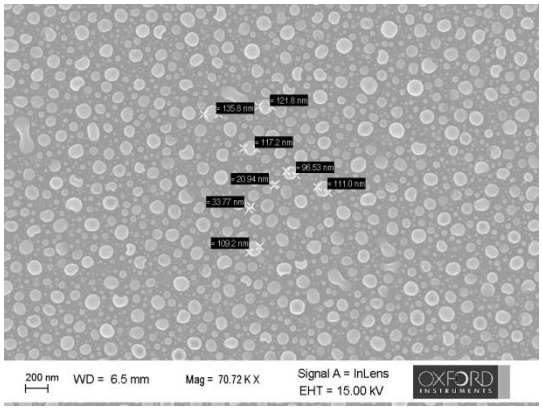


Fig. 1 shows SEM images of ITO/Si structures after H plasma treatments at 100 ° C for 10 min.These NPs can be used for some applications: (i) as local conductive channels in some advanced solar cell structures; (ii) as seeds for the growth of Si NWs by VLS methos. Indium based NPs were intensively tested for the processing of HJ solar cells in WP5.

Fig. 1: SEM images of ITO/Si structures after H plasma treatments for 10min

Nanoparticles for processing of local contacts/conductive channels

The following methods, which can be used for the formation of nano-contacts/conductive channels, have been developed in frame of the nanoPV project:

- Synthesis of metal contacts using hydrogen initiated reduction of ITO layers.
- Synthesis of conductive channels in nanolaminate dielectric structures.
- Synthesis of nano contacts using sol-gel and laser ablation methods.

As a result, the following nano/micro contacts can be used for an conversion efficiency enhancement of Si based solar cells: (i) In/Sn obtained by the hydrogen initiated reduction of ITO layers; (ii) conductive channels formed in nanolaminate dielectric structures and (iii) Ag nano-particles obtained using sol-gel and laser ablation methods.

All mentioned above methods for fabrication of nano/micro contacts have been tested for the processing of relevant Si based solar cell structures during the second period of the project.

An innovative approach has been developed by CLS. The idea is to use an electronic conductivity in granular materials. The granules are arrays of metallic particles of sizes ranging usually from a few to

hundreds of nanometers embedded into an insulating matrix. Granular arrays can be treated as artificial solids with programmable electronic properties. The ease of adjusting electronic properties of granular metals assures them an important role for applications.
Technological approach: the multilayer structure is formed using one or two different dielectrics. The electrical conductivity is modified with planar located metal granules. Sheet resistance has been measured using the four-point probe method, Transmission Line Method (TLM), van der Pauw method and I-V measurements of the resistors. The studied samples are nanolaminate dielectric structures on the thermally oxidized silicon wafers. Four- point probe method and transmisssion line method gave the following number for the sheet resistance R_{sh} = 5-7 Ohm/sq. Results from van der Pauw metod: the electrical resistivity of the conductive area at room temperature is $\rho = 9.\ 9\ 10^{-5}$ Ohm·cm. Conductive areas with different forms and sizes can be formed on nanolaminate dielectric structure with the help of template mask or photolithography after additional treatment.
The electrical conductivity is studied depending on the type of the dielectric used and on the thickness of the dielectric layers in this nanolaminate structure. Good conductivity can be obtained for nanolaminate structures with dielectrics such as SiO_2, TiO_2, ZrO_2, Al_2O_3 and $(Al_2O_3)_x(B_2O_3)_{1-x}$, deposited as a first layer on substrate (”bottom” layer of the nanolaminate structures). It can be concluded that innovative types of nanolaminate structures discussed above can be considered as a promising approach for processing of low-cost Si based solar cells.

Metal nanoparticles and related layers for plasmonic effects

Though plasmonics is a wide area of study, its application in the field of solar cells has recently attracted a great attention. Metals in general support surface plasmons that are collective oscillation of excited free electron and characterized by a resonant frequency. The resonances of noble metals are mostly in the visible or infrared part of the spectrum, which is of interest for photovoltaic applications. It is demonstrated that metallic nanoparticles (Au, Ag, Cu) and related layers, which exhibit plasmon resonance, can be formed using magnetron sputtering (or co-sputtering) of thin layers followed by an annealing step at temperatures in the range 300-600 °C. In situ synthesized Au and Ag NPs in thin layers of SiO_2 and TiO_2 on Si wafers can be formed using spin coating. ESAVD (electrostatic spray) can be used for the processing of SiO_x layers containing Ag NPs. Metal NPs have been intensively tested in WP5 related developments.

Pre-assessment application of nanotechnologies for processing of related solar cells

The key conclusions from the pre-assessment application of nanotechnologies for processing of related solar cells that could result in cell efficiency gain are listed below:

- Microcrystalline or rather nanocrystalline emitter layers are compatible with high efficiency heterojunction solar cells. For this approach it is crucial to introduce a nanometer-thin intrinsic amorphous buffer layer at the emitter as well as at the BSF side of the solar cell. Further increase of efficiency is to be expected when building a µc-Si(p)/a-Si:H(i)/c-Si(n)/a-Si:H(i)/a-Si:H(n+) solar cell with optimized TCO and antireflective/scattering layers/textures.
- Highly crystalline silicon nanodots embedded in a SiO_2-matrix were successfully grown onto oxidized c-Si wafers and effective doping of those nanodots has been realized. It has been found that SHJ solar cells with silicon nanodot/silicon oxide emitter exhite rather low efficiencies and these development have been put on hold.
- SiO_2:Tb films have demonstrated absorption in the UV range (224 nm) of the solar spectrum and photoluminescence in the visible range (~ 550 nm). First tests of application as a down-convertor in poly-Si thin films solar cells have been reported. Poly-Si thin film solar cells with this type of SiO2:Tb

films directly deposited on top of the TCO layer have been processed. Initial tests carried out without any optimisation of the deposited ZnO/NRs stack with respect to ARC show an increased EQE in the UV region, which is the desired effect of down conversion in those cells. However the overall effect is a slight decrease in short circuit current since the stack needs to be further optimized not only for down conversion but also for ACR in future experiments.

- Al_2O_3 with Ag + Cu nanoparticles after annealing exhibit better properties for plasmonic application to solar cell – more pronounced plasmonic peak of absorption for samples annealed at 500^0C, the transparency is higher than 95% and the values of reflection are lower in the wave range 400-1000 nm.
- Multilayer structures such as Al_2O_3(70nm)/Ag(12nm)/Al_2O_3(50nm) and ZnO:Al(70nm)/Ag(12nm)/ZnO:Al(30nm) exhibited potential for solar cell application.
- CdSe/CdS Core/Shell nanorods (NRs) possess very high PL quantum yield (~60%) and very large quasi-Stokes shift between absorption and PL band maxima (~100 nm), which made these NRs promising for spectrum down-conversion.
- ESAVD produced Ag nanoparticles in SiO_2 have shown to exhibit plasmonic effects. The cell parameters can be optimised further by tuning the content, size and shape of the nanoparticles further in such a way that the system is optimized for the rear side of the cell.
- Nanolaminate structures have been explored and tested as nano-thin transparent back side electrodes with local contacts providing at the same time good passivation for mc-Si or c-Si solar cells. Further optimizations are required to implement such structures for the processing of Si based solar cells.

Assessment application of nanoparticles to solar cells

The main conclusions with respect to the assessment of the application of nanoparticles to solar cells are:

- Plasmonic layers, applied on the front side of solar cells may not be the optimal choice. In the case of Au nanoparticles in TiO_2, deposited on Si wafer based cells, the absorption at the localized plasmon resonance decreases the photocurrent of the solar cell. Besides that, the layer reduces the passivation quality of the interface, which can be improved by introduction of an intermediate passivation layer.
- Nanoparticle emitter formation by nano-/microcrystalline emitter (µc-Si/a-Si:H/c-Si solar cell) with an a-Si(i) buffer layer, has led to a V_{oc} of 689 mV, which is a very promising result. On SHJ cells with a phosphorus doped silicon nanocrystal emitter and a-Si(i) buffer layer, a high implied V_{oc} of 700 mV is achieved.
- Spectral conversion layers of CdSe/CdS nanorods show an enhanced response in the blue spectrum, which proves the principle. However, absorption in the longer wavelength spectrum reduces the effect. Directly applied on a different cell sample, the same particles resulted in only 0.5% current loss, which indicates that it is necessary to tune properties of such layer further to achieve current gain.

Conclusions

It is shown that in most cases implementation of NPs for Si solar cell processing requires essential modification of the solar cell processing steps and not always properties of individual nanoparticles and relevant layers can improve properties of Si based solar cells. Nevertheless, nanoPV consortium selected most promising NPs based structures, which potentially can result in an enhancement of Si based solar cell efficiencies.

NANOWIRES AND RELATED SOLAR CELLS

Work on this topic was part of WP2. In this WP, Cost effective methods for fabrication of nanorods and related solar cell structures are developed: All silicon, TCO, and metallic based nanorods on highly conductive substrates (metal, highly doped low-cost Si substrates) with the diameter of NRs below 200 nm and methods for their incorporation into the solar cell structures are developed. Several processes and approaches are used: (i) bottom-up using vapor-liquid-solid, electrodeposition assisted by low-cost template based methods, (ii) top-down alternative route based on electroless metal-assisted etching of low-cost Si thin layers deposited on low-cost conductive substrates, (iii) vacuum and non-vacuum low-cost methods for fabrication of bottom-up and top-down 1D ZnO and TiO_x based structures for implementation as ARCs in conventional Si (thin film and wafer based) solar cells, (iv) cost effective bottom-up processes for formation of metallic 1 D based structures, which can be used as substrates for advanced thin film based solar cells. Methods for nanotexturing of Si substrates are developed and evaluated.

This WP has the following objectives:

- To fabricate individual Si and TCO based nanorods with desired optical and electrical properties, composition etc.
- To develop methods for effective passivation of Si nanorods
- To optimize processes for incorporation of nanorods into solar cell structures (route 1)
- To develop cost-effective non-vacuum and vacuum based processes and equipment compatible with industrial requirements for the implementation of Si (route 2) and TCO nanorods (routes 1,2) for solar cells
- To develop optimal process for nanotexturing of wafer and thin film Si substrates to obtain "black, light-trapping silicon" with high electronic quality and technological compatibility with the standard processes of solar cell manufacturing (route 1)
- To develop processes for merging of 0-D and 1-D nanostructures for fabrication of advanced solar cell structures in frame of routes 1 & 2

Silicon nanorods/nanowires synthesis

Silicon nanorods have been prepared in a bottom up approach by VLS growth and in a top down approach by etching. In both cases, axial as well as radial pn-junctions were fabricated to get Si nanowire solar cells (route 2).

For the VLS growth as substrates silicon wafers, laser crystallized multicrystalline silicon thin films as well as TCO layers (aluminum doped zinc oxide) have been used. As a nanotemplate for the VLS growth a 2 nm thick gold films was evaporated on the substrate layer from which nanodroplets were formed by annealing. VLS growth was performed at about 630 °C from silane to result in several µm long nanowires with a diameter in the range of 50 to 100 nm. For doping the nanowires, doping gases were added to silane (diborane B_2H_6 for boron doping or phosphine PH_3 for phosphorus doping). The growth rate was about 300 nm/min. NW solar cells were prepared based on these nanowires, both following the axial and radial heterojunction concepts. In the reporting period, regarding the VLS-grown NWs we mainly worked on the embedding and contacting of axial heterostructure NW solar cells. However, we did not reach a satisfactory level now, especially envisaging the removal of the topmost layer of the capping material to successfully contact the NWs. Combination of axial and radial junction solar cells grown by a combination of thermal CVD and PECVD has been investigated. In this concept, we try to reach a combination of axial and radial junction by first growing a NW by thermal CVD and in a second step

growing an intrinsic as well as an oppositely doped top part onto this NW by PECVD. PECVD results in the deposition of a-Si on the NW's surfaces, so that a radial p-i-n junction will also evolve.
Nanowire solar cells prepared by etching were investigated on wafers and on polycrystalline (pc-Si) silicon on glass substrates. The best solar cell with nanowires, etched in to Si wafer, showed a V_{oc} of 517 mV and an efficiency of 10.0%. For nanowire solar cells on polycrystalline thin films, the pc-Si was prepared from electron beam evaporation (EBE) deposited a-Si followed by CW diode laser crystallization. Etching was done by $AgNO_3$/HF solutions. Based on etched nanowires, radial pn-junction nanowire solar cells were prepared on the pc-Si thin film. It was observed, that the solar cells showed better performance in superstrate configuration than in substrate configuration. The best cell so far on a 8 µm thin pc-Si thin film reached, in superstrate configuration, V_{oc} of 520 mV, j_{sc} of 28.1 mA/cm², fill factor of 68.4%, and efficiency of 10%. With this result, the main aim of this task has been achieved.
Regular silicon nanowire arrays were prepared by nanosphere lithography on silicon wafers and on crystalline silicon thin films on glass substrates as sketched in **Fig. 2**. The c-Si thin films were prepared by diode laser crystallization of electron beam evaporated amorphous silicon films, deposited on borosilicate glass substrates. For the nanosphere lithography first a monolayer of polystyrene spheres was prepared on the silicon substrate by a Langmuir-Blodgett technique.

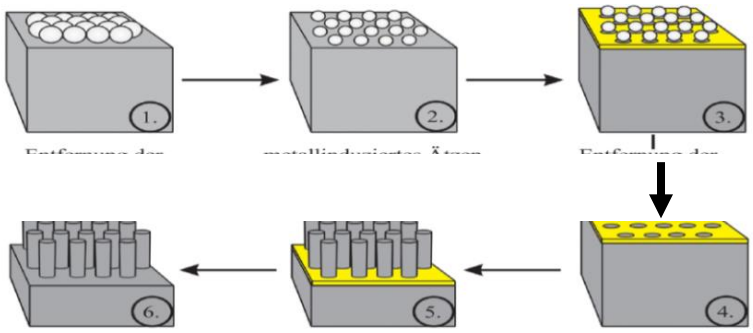


Fig. 2: Steps for preparing regular nanowire arrays

To this end, 0.6 and 1.03 µm diameter spheres suspended in water were used (microParticles GmbH). To 100 µl of the suspension 100 µl ethanol and 5 ml hexylamine (5%) were added and sonicated for 30 min. The samples were placed on a pedestal in a glass bowl filled with DI water. A drop of the nanosphere suspension was added. To get a monolayer of nanospheres on the water surface, several drops of sodium dodecyl sulfate solution (10%) were added. The surfactant pushes the nanospheres together. Finally the water level in the dish was lowered by a hose. In this way the nanosphere monolayer on the water surface settles on the substrate. **Fig. 3** shows an SEM image of a nanosphere array prepared in this way.

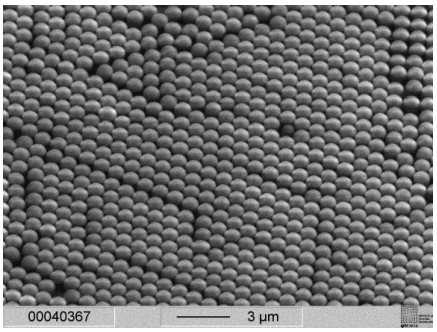
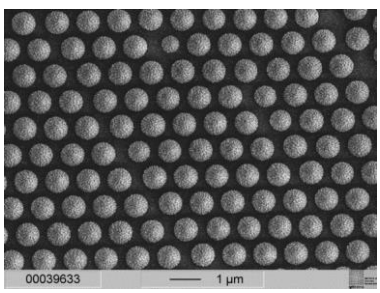


Fig. 3: 1.03 µm diameter nanosphere array on a silicon substrate

In a next step the diameter of the nanospheres is reduced by etching in an oxygen plasma (**Fig. 4**). The final size of the nanospheres can easily be controlled by the etching time.Onto the samples a 50 nm thick silver layer was deposited by evaporation. The silver covered nanospheres were removed by sonicating the sample in a mixture (10:1) of methanediol and acetone. As a result a silver mask remained on the silicon surface (**Fig. 5**).



Nanowires were prepared by metal assisted etching using a mixture of $HF:H_2O_2$ (20:1). Silicon is etched below the silver mask to result in a regular array of nanowires as shown in **Fig. 6**.

Fig. 4: Nanosphere array after 120 s plasma etching

The regular nanowire arrays on silicon thin films were optically characterized. The results are described in WP4. Moreover, solar cells with radial pn-hetero-junction were prepared in way similar as in case of irregular nanowires. **Fig. 7** shows a SEM top and side view of the final solar cells based on regular nanowire arrays.

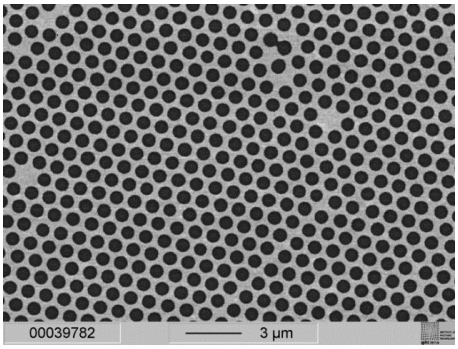


Fig.5: Silver mask

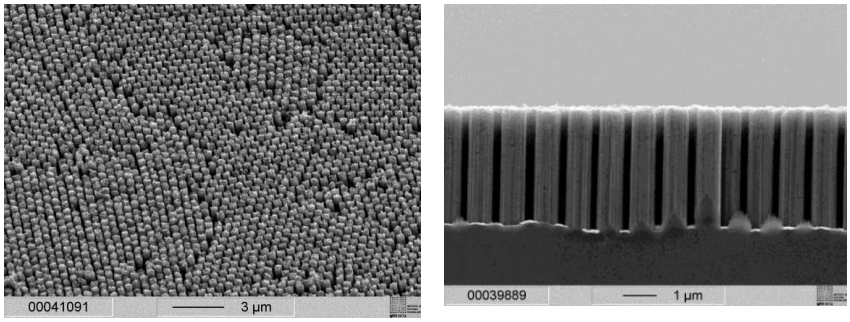


Fig. 6: Regular nanowire array on a silicon thin film on glass (left) and on a wafer (right)

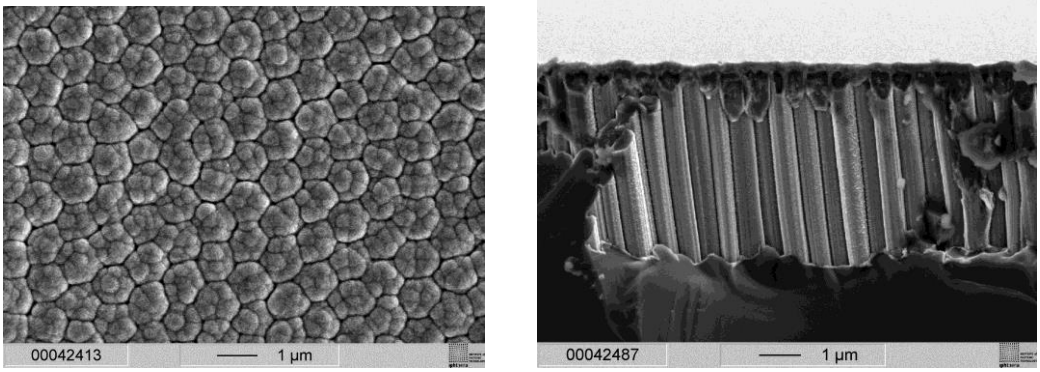


Fig. 7: SEM top view and cross section of a solar cell based on regular nanowire arrays

Fig. 8 shows the I-V curve of a solar cell prepared on a regular silicon nanowire array. An efficiency of 5% was reached, which is somewhat lower that reached in irregular arrays. Particularly the open circuit voltage is a bit low. However, in case of regular arrays much less optimization efforts were done.

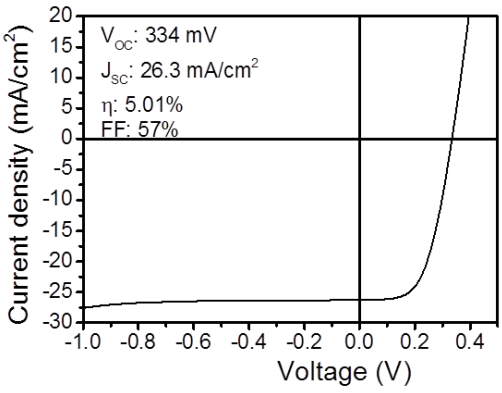


Fig. 8: I-V curve of a solar cell based on a regular silicon nanowire array

Growth of Si nanowires by thermal CVD and PECVD processes has been done to develop f novel structures of silicon nanowire based solar cell. Al, Au and ITO reduced by H plasma treatments were used as catalysts for the preparation of Si nanowires and junctions.
Fig. 9 shows the p-n junction obtained from ITO catalyst on Al substrate and Si substrate. The red arrow in **Fig. 9** points

to the p-n junction area, which results from different shape of Si nanowires for p-type and n-type. The purple arrow indicates a 3D structure of Si NWs. Similar structures have been observed in Au/Si and ITO/stainless steel.

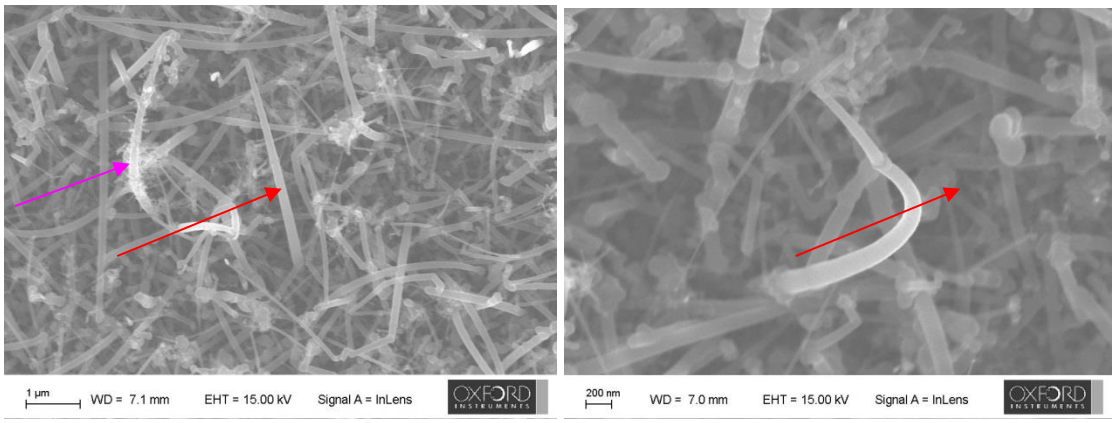


Fig. 9: p-n junction and 3D structure obtained using reduced ITO as a catalyst

Electrochemical deposition of ZnO NW as ARC on Si solar cell structure and (Si solar cell structure)/ITO

Development of low-cost processes for the fabrication oxide based nanostructured (ZnO) by electrochemical deposition to be implemented as anti-reflective coatings (ARC) for the fabrication of conventional Si based (thin film and wafer based) solar cells. Experiments of deposition of ZnO NW as ARC were performed on c-Si solar cell structures with ITO ARCs. Two different types of solar cells have been studied - with and without textured surface before the deposition of ITO. ZnO nanostructured layers are deposited by electrochemical method on the front side of the solar cell structures. Optical and structural properties of the deposited structures were studied.

SEM images (with different magnification) of the surface of electrochemically deposited ZnO on the top of the solar cell with textured front side surface are presented in **Fig.10.** ZnO nanowires with hexagonal shape have been grown on different side of the pyramidal etched surface of the solar cell.

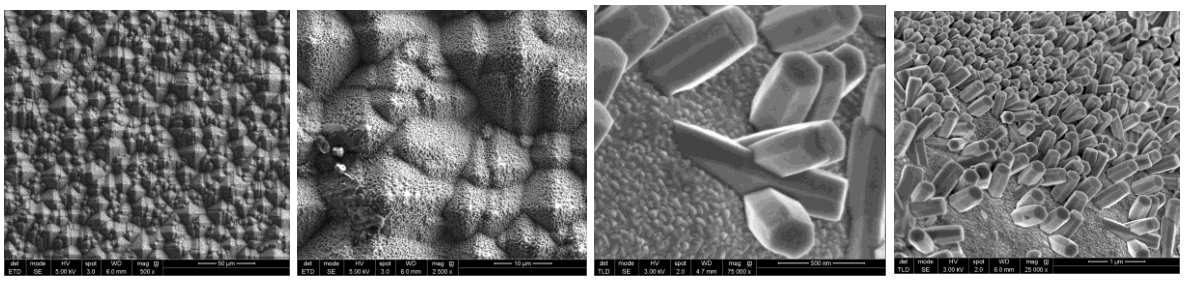


Fig. 10: SEM images (with different magnification) of the surface of electrochemically deposited ZnO on the top (textured surface) of the solar cell (ITO/n+-Si (~0.4µm, emitter)/p-Si – base, ~200µm/p+ Si – BSF) are presented The ZnO was deposited for 20 min.

Fig. 11 shows the spectra of reflectance and diffuse reflection for c-Si solar cell structure)/ITO. Solar cell structures are: ITO/n+-Si (~0.4 µm, emitter)/p-Si – base, ~200 µm/p+ Si – BSF, ~2 µm without metal

contacts. The front side of the solar cells is textured. ZnO layers are deposited for different times. The spectra of solar cells structures before deposition of ZnO are given for comparison as well.

Electrochemical deposition of the ZnO results in decreasing of the intensity of the band of reflectance at about 400 nm by about 10% and slightly increase (about 0.2%) of the diffuse reflection in the range 550-100 nm compared to the value of the based structure: ITO/Si solar cells. Applying deposited ZnO on the surface of the solar cell can increase generation of the carriers and the value of the photocurrent in the spectral range 400-480 nm, but a decrease in the visible range occurs. Optimization of deposition process and ZnO NWs structures are still required.

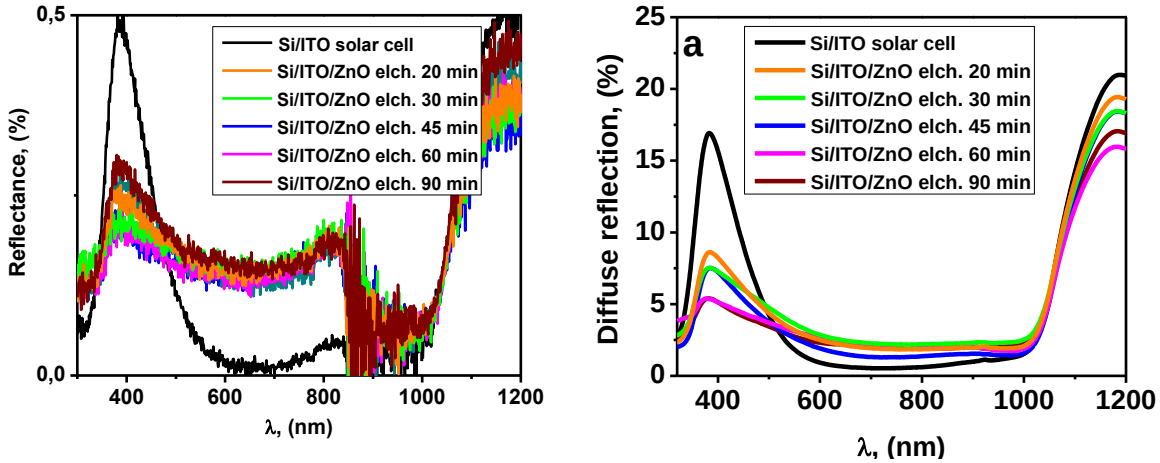


Fig. 11: Spectra of reflectance and diffuse reflectance for structures ITO/n+-Si (~0.4 µm, emitter)/p-Si – base, ~200 µm/p+ Si – BSF (untextured surface) with ZnO deposited for different time.

Results, concerning TCO NWs obtained in naoPV project can be summarized as follows: ZnO nanowires useful as antireflection layers on solar cells were successfully prepared by electrochemical deposition, by spray pyrolysis, by CVD, by low temperature non-vacuum deposition, and by etching.

Nano-texturing of silicon substrates

Modified nano-textures, with life-time of the photo-generated carriers up to 500 µs, have been obtained by applying SC1 post-treatment to the nano-texture. This value is approaching the threshold level, required for high quality back contact solar cells. Further improvement of the electronic quality of c-Si nano-textures has been achieved by a-Si:H passivation.

During the implementation of black nano-texture to actual solar cell structures the nano-texturing process has been continiously improved. Important particular achievements are: (i) a modified procedure for black etching of poly-Si thin film absorbers (for HZB) has been developed. This procedure results in strong reduction of reflectivity, as well as in ultimate light-trapping within the thin absorber due to enhanced, difractive scattering in size-optimised nano-texture; (ii) the standard black etching process has been developed to work also with highly doped Si substrates with donor (acceptor) concentrations up to 10^{18} cm^{-3}. This allows integration of black nano-textured surfaces in highly doped regions of a large variety of prefabricated solar cell structures in route 1; (iii) a new, buffered, black etching solution has been developed, which works even with more heavy doped Si. Substantial advantage of this solution is that nano-texture with desired morphology and optical properties is obtained without additional post-treatments, which are otherwise necessary with the "standard solution" that was used earlier (**Fig. 12**). The new buffered solution also do not destroy photoresist protective layers in contrast with the "standard solution". This expands significantly the technological flexability of the nano-texturing process.

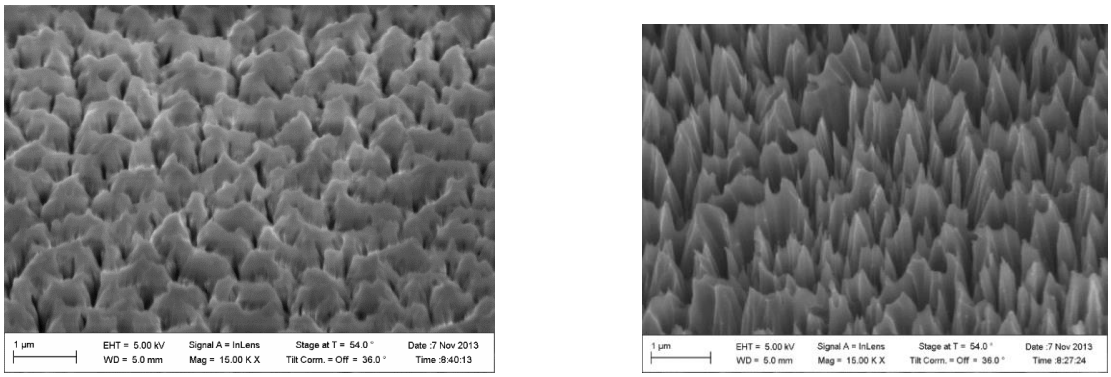


Fig. 12: Comparison of the nano-textures as prepared by a)"standard" black etching and b) "buffered" black etching.

The scalability of the metal-catalized black etching to wafers of industrial scale in batch processing has been demonstrated for all developed versions of the nano-texturing process. Obtained results can be summarised as follows: black etching of silicon was successfully extended to highly doped wafers and to polycrystalline silicon thin films. The material shows very low reflectance and enhanced absorption as expected. On wafers the carrier lifetime could be extended to 0.5 ms and with highly efficient a-Si:H passivation above 1 ms. Thus, excelent optical and electronic quality of the nano-textured sssilicon surfaces have been achieved. These surfaces fulfill all the requirements for successful application in photovoltaic solar cells.

Development of the advanced equipment for the processing of Si based solar cells using nanotechnology approaches

The hardware tests and process verification has been done as specified for the task:

(i) It is tested that Si NW pn-junction is possible to be done in a single chamber when the hardware performance is correct. As an example for the easy identification, the thermal CVD intrinsic layer and PECVD for p layer of Si NWs is prepared. **Fig.13** shows that Si NWs grown by pure thermal CVD have the same diameter along the length of nanowires with the length of about 0.9-1.4 µm, and the PECVD grown Si NWs show tapered shape and the length is 1-1.3 µm.

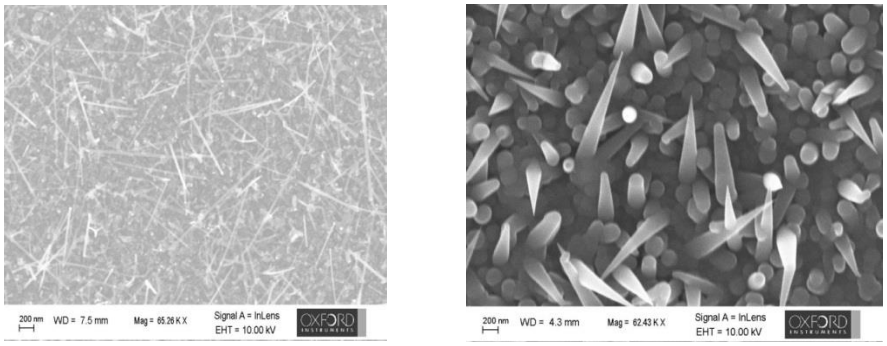


Fig. 13: SEM images of silicon nanowires grown by thermal CVD (left) or PECVD (right)

(ii) Development of a single chamber/cluster system process based on deposition of thin metal catalyst layer followed by an in situ anneal and VLS growth of Si NWs. This part of verification was performed in two separate cases:

Case 1: The catalyst layer (Al) has been deposited at different temperature, or annealed after the deposition, as shown in the following SEM images (**Fig. 14**). It has been demonstrated that when catalyst layer is deposited at room temperature, it needs to be annealed at high temperature for the formation of nanoparticles, whereas the temperature of the table can be lower when the table is heated while the deposition is performed;

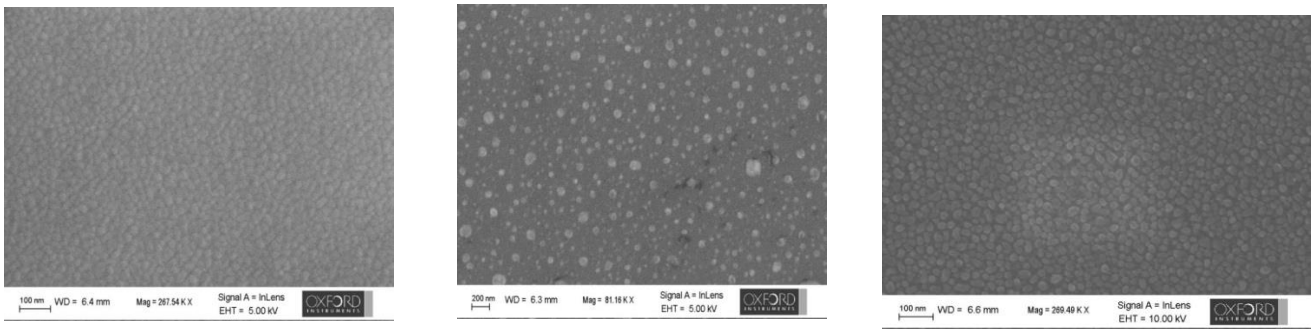


Fig. 14: 10 nm Al layer on Si substrate deposited at room temperature (upper left) and after anneal at 600 °C (upper right) showing the formation of Al nanoparticles. 10 nm Al layer deposited at 400 °C (bottom, left).

Case 2: the catalyst can be annealed in the chamber that is used for the growth of Si NW and then Si NWs can be grown. Au nanoparticles can be formed in the process chamber, which then can be used for the growth of Si NWs by CVD or PECVD, as shown in above SEM images.

(iii) Combination of Si NRs/NWs growth and a-Si PECVD
(iv) Si/SiO_x multilayers plus annealing for nanodots

IMPT contributed to this task with the unique non-vacuum equipment for the deposition of TCO based nanostructures layers. IMPT hardwares have been optimized on the basis of feedbacks obtained from NanoPV partners (especially HZB and ECN) with the characterized nanomaterials and related solar cell structures processed with this equipment. Process and related equipment developments that underpin reliable process delivery have been performed within the following strategy by IMPT: (i) verification and development of heater and module for the deposition of ZnO seed layer for the grown of ZnO nanorods; (ii) module for the deposition of nanowires based TCO plus low temperature *in-situ* annealing.
The cost-effective non-vacuum based processes and equipment with the relevant modules compatible with industrial requirements for the implementation of TCO nanorods (routes 1 & 2) for solar cells have been developed by adapting the *in-house* dedicated Electrostatic Spray Assisted Vapour Deposition (ESAVD) for the deposition of nanomaterials in NanoPV project. **Fig. 15** shows the advanced prototype equipment developed for the processing of Si based solar cells using nanotechnology approaches.
Both non-vacuum low-cost methods for the processing of Si-based solar cells using: a) bottom-up; and b) top-down have been established.
The ESAVD tool can be clustered with other tools or modules for continuous or in-line production processes using top down and bottom up approaches.

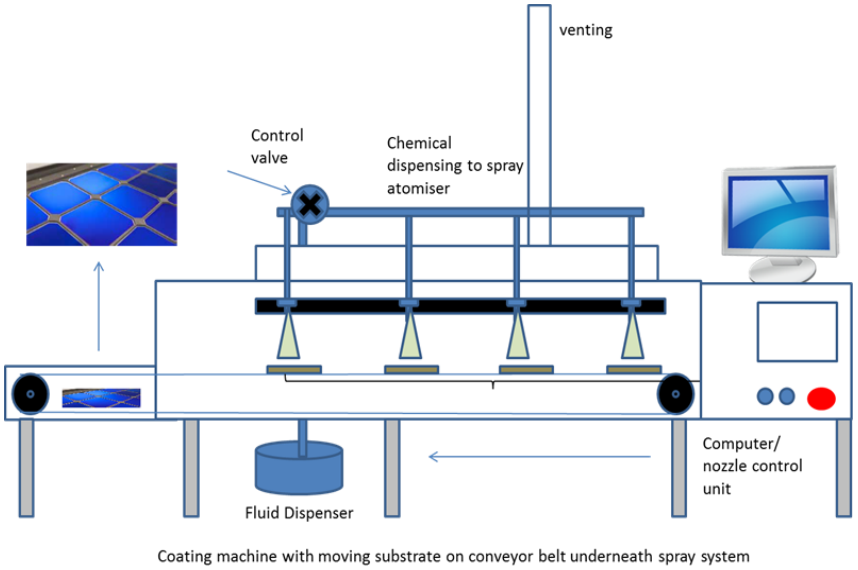


Fig. 15: The layout of ESAVD equipment for the processing of Si based solar cells using nanotechnology approaches.

Proof of principle of application of nanorods and nanotexturing to solar cells

The overall progress in this activity can be summarized as follows:
Silicon nanowire solar cells were prepared with an efficiency of up to 10% on polycrystalline silicon thin films on glass. Black etching of silicon wafers reached a quality concerning low reflectance and surface passivation that it can be used in solar cells to reach 15% efficiency on n-type Si wafers. With the HIT concept, even an efficiency of 17.2% was reached using black etching. Black etching of polycrystalline silicon layers was shown to be promising. The efficiency of HIT solar cells could be improved by ZnO nanostructures on top by up to 0.4% absolute, which was due to reduced reflection and increased short circuit current. TCOs with inserted Ag nanowires, deposited at low temperature, were tested.

Conclusions

Significant results obtained in WP2:

- Silicon nanowires were etched into low cost substrates such as crystalline silicon thin films on glass.
- Silicon nanowire solar cells etched into wafers which are based on a-Si heterojunction reached 10.0% efficiency.
- Silicon nanowire solar cells etched into polycrystalline silicon thin films on glass, with a radial pn-heterojunction, reached 10.0% efficiency (see project objectives).
- Regular silicon nanowire array was prepared by nanosphere lithography and their optical properties were determined. First solar cells on these structures reached an efficiency of 5%.
- TCO nanorods were prepared as antireflection layers by electrochemical deposition and by RIE. By adding these structures to HIT solar cells, their efficiency could be improved by 0.4%.
- On black etched wafers the carrier lifetime could be extended to 0.5 ms and with highly efficient a-Si:H passivation above 1 ms. On n-type wafers an efficiency of 15% was reached, with HIT concept even 17.2%.
- Metallic nanorods were prepared by electrochemical deposition into AAO porous membranes

ULTRATHIN NANOLAYERS AND RELATED SOLAR CELL STRUCTURES

Work on this topic was part of WP3. In this WP, cost effective vacuum and non-vacuum based methods for fabrication of ultrathin nanolayers and related solar cell structures have been developed. The developed processes have been used as a background for innovative technologies based on an implementation of nanolayers in PV. Manufacturing procedures and optimized equipment for the processing of nanolayers compatible with industrial requirements have been developed in WP3. Several alternative methods have been developed for the cost-effective production of such nanolayers: (i) electro-deposition, (ii) ECR-PECVD, (iii) low-temperature oxidation, magnetron sputtering, (iv) ESAVD. The results have been evaluated based on comprehensive innovative and elaborated analytical techniques.

Si nanodots in SiO_2 and Si3N4 matrixes as nano emitters

Si-nanostructures have been fabricated by decomposition of amorphous SiOx layers. The layers have been optimized with respect to nanodot formation for different O/Si-ratios between 0 and 2 have and annealing temperatures of up to 1000°C. In agreement with previous studies the following details with respect to nanodot formation and properties could be confirmed: For completing the decomposition temperatures of around 900°C are needed. The size and density of the nanodots decreases with decreasing O-content and nanodot diameters between 5 and 10 nm can be reached. For higher O-content a blue-shifted PL signal can be observed, indicating quantum size effects within the sample. Furthermore an effective doping of the nanodot layers could be obtained as evidenced by SPV and current-voltage measurements. Both for n-type and p-type doped nanodot layers on p-type/n-type substrates a band bending of up to 700mV could be proven by SPV. This opens the possibility for applying those layers as an emitter in solar cells. For the first time such a nanodot layers have been used as an emitter for a solar cell based on a poly-Si thin film absorber. Open circuit voltages of ~400mV could be reached which are comparable to poly-Si thinfilm solar cells with conventional emitter. Possible advantages of such an emitter include a high temperature stability which is needed during poly-Si thin film formation and a high optical transparency. For application in wafer based solar cells a higher interface passivation would be needed and thus a temperature stable passivation layer. Possibly those layers could be combined with an ultrathin, tunneling, passivation plasma oxide layer which have already been tested as passivation layer which can survive subsequent high temperature steps.
Several altternative nano-emiters have been developed in frame of WP3: (i) SiOx and Si NDs in SiNx and SiCx structures nano-emitters and processed by magnetron sputtering; (ii) Si nanodots on Si surface or in SiO_2 and Si_3N_4 matrices by e-beam evaporation. In all cases, further optimization of nano-emitters is required.

SiO_2 layers for tunneling and passivation

Several technologies for processing of ultrathin SiO_2 layers have been developed: (i) plasma oxidation; (ii) Wet-chemical oxide as ultrathin tunneling, passivation layer in SHJ solar cells; (iii) sol-gel deposition of thin SiO_2 films as passivating layers; (iv) ultra-thin SiO2 passivation layers by ALD; (v) ultrathin SiOx layer formed at the interface of ITO/Si. All mentioned above SiO_2 layers have been tested for the processing of solar cell structures and can be considered as promising options for the cost effective Si based PV.

Passivation by alternative oxides

TCO based layers deposited by ALD based methods: for the silicon nanowire solar cells according to the radial pn-junction concept as sketched in **Fig. 16**, a TCO layer is required as a contact to the a-Si shell. In

order that the TCO layer fills the space between the nanowires, deposition has to be conformal, even in the deep and narrow grooves between the nanowires. To achieve this, atomic layer deposition is perfectly suited, whereas the more conventional sputtering technique is not useful. For the concept of n-type nanowires and p-type a-Si:H emitter as a shell, a good contact between TCO and p-type silicon is needed. Aluminum doped zinc oxide (AZO) is well suited for that. For ALD deposition of ZnO, consecutive gas pulses of diethyl zinc (DEZ) and water are introduced into the device, separated by neutral gas flushing. For doping, every 15th to 30th (DEZ) pulse is replaced by a trimethyl aluminum (TMA) pulse. Optimization was done with respect to the Al:Zn ratio and the deposition temperature.

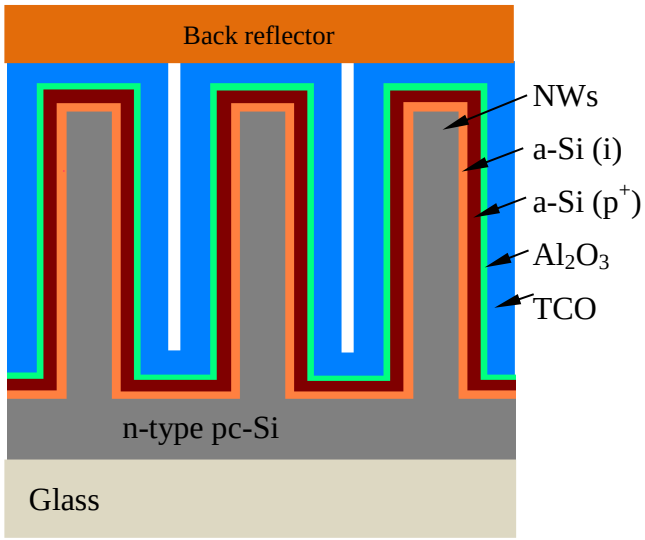


Fig. 16: Concept of silicon nanowire solar cell

Moreover, several types of other oxides have been tested in frame of nanoPV; (i) TCO based layers deposited by ESAVD based methods; (ii) sol-gel deposition of thin Al2O3:B2O3 films as passivating layers; (iii) ultrathin Al2O3 films as tunneling, passivation layer by ALD. All mentioned above layers (except TCO) exhibit good passivation properties and can be used for processing of Si based solar cells.

Nanolayers with nanoparticles

Several types of nanolayers with nanoparticle have been processed and tested: (i) nanolayers with nanoparticles fabricated by chemical liquid deposition; (ii) Ge, Au nanoparticles by means of e-beam deposition on top of oxide layers (SiO_2, HfO_2); (iii) ITO layers with In NPs. N-type epi-Si(30 µm)/n+ Si substrate structure has been used to process HJ solar cells. Ultrathin Al_2O_3 passivation tunnel layer between AZO and a-Si:H emitter have been employed. Nanotexturing of the AZO layer through etch back has been done. J_{sc} of 30.3 mA/cm^2 determined by small cell cut from large piece with edge passivation. The following results have been obtained: Results: Improved V_{OC}: 618 mV, J_{SC}: 30.3 mA/cm^2 FF_P: 81.1%, η_p: 15.2%

Proof of principle of application of nanolayers to solar cells

Solar cells involving nanolayers with nanoparticles. Within WP3 several concepts for solar cells with nanolayers containing nanoparticles have been investigated. All concepts are based on silicon heterojunction solar cells and on the application of nanoparticles inside the stack of a-Si:H nanolayers that form the emitter (**Fig. 17**).

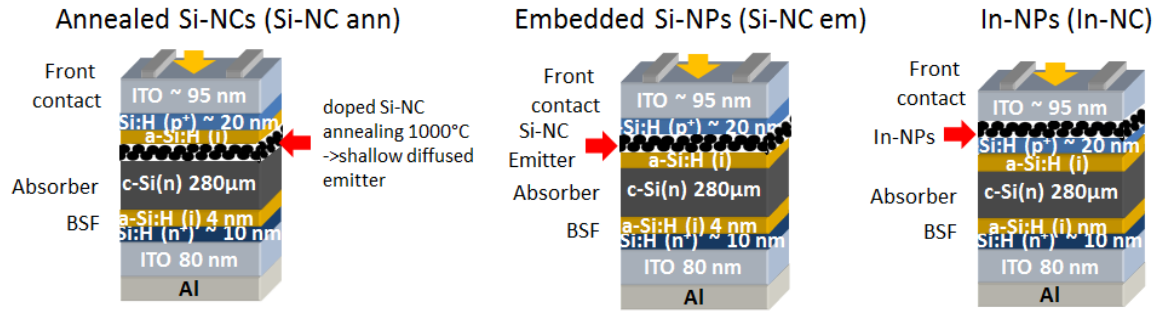


Fig. 17 Heterojunction solar cells with Si NPs.

In summary a slight increase of conversion efficiency of silicon heterojunction solar cells could be obtained by introducing nanoparticles to ultrathin emitter layers, albeit that the conversion efficiency of the reference solar cells where not on a top level (η=15.2%). The efficiency increase up to η=16.4%, obtained for solar cells involving In-NPs processed from ultrathin ITO layers and sandwiched in between the ultrathin a-Si:H emitter and the ITO front window layer, stems from a slight increase in Voc and an increase in short circuit current. While the Voc could be increased due to the additional H-plasma treatment which was performed to create the In-NPs, the increase in current must be attributed to the In-NPs themselves, which cause increased internal quantum efficiency in the short wavelength range. Furthermore, silicon heterojunction solar cells with Si-NCs embedded in ultrathin a-Si:H emitter layers have been developed and conversion efficiencies of η=15.2%, on the same level as the reference solar cell, have been obtained. Such high efficiencies can only be reached if an ultrathin intrinsic a-Si:H buffer layer is present between the absorber and the Si-NCs to passivate the interface defects and suppress recombination such that high open circuit voltages >700 mV can be reached. The short circuit current of such solar cells are slightly increased due to slightly reduced reflection on planar wafers and slightly increased internal quantum efficiency on textured wafers. The high internal quantum efficiency indicates that the light absorbed in the Si-NCs generates charge carriers that can be extracted from the solar cells. This opens up new perspectives for applying those nanoparticles embedded in ultrathin emitter layers. At the current stage of development the solar cells with Si-NCs suffer from a low fill factor, due to a high serial resistance which is presumably due to an oxide shell surrounding the Si-NCs.

Finally it has to be noted that the overall low level of conversion efficiency can largely be attributed to sample contamination during transport between laboratories and sample shipment. Reference solar cells processed at HZB that undergo the routine process flow reach conversion efficiencies of up to 20%. For the final solar run with solar cells involving In-NPs special attention has been paid to fast sample processing and special protection of solar cells during shipment and solar cell efficiencies of 18.4 % have been reached (see description of WP 5 activity). Several other solar cell structures with ultra-thin oxides have been tested: (i) ALD-Al2O3 integration in n-Pasha solar cells; (ii) (Al2O3)x(B2O3)1-x passivation layers for rear side of c-Si solar cells; (iii) Solar cells involving a nanodot emitter (Si NPs in SiOx). In all cases rather promising results have been obtained, but high efficiencies for solar cells were not reached, which indicated that further technological optizations are required.

Conclusions

Significant results obtained in frame of WP3 can be summarised as follows:

- Indium based NPs, obtained by the reduction process of ITO initiated by H+ plasma have been fabricated and it has been concluded that they could be combined with a-Si:H emitters to form high

conductive channels at ITO/a-Si:H interface. Solar cells based on this concept have been processed and conversion efficiencies are higher than the reference and reach 18.4 %.

- Heterojunction solar cells with a-Si:H emitters incorporating Si-NCs have been processed by HZB and conversion efficiencies of 15.2 % have been reached, which is on the same level as the reference solar cell. The high internal quantum efficiency indicates that the light absorbed in the Si-NCs generates charge carriers that can be extracted from the solar cells.
- Ultrathin a-Si:H layers for the passivation of nanotextured silicon surfaces have been developed. It was shown that it is possible to passivate nanotextured silicon surfaces of different pre-etching crystallographic orientations with a-Si:H and to reach very high effective charge carrier lifetimes of 1.3 ms. Heterojunction solar cells (wafer and thin film) with ultrathin layers for the passivation of nanostructures have been processed by and conversion efficiencies of 17.2 % have been reached (WP5).
- AL2O3 passivation layers have been optimized and applied for passivation of black-Si textures in IBC solar cells and for the passivation of the backside in in n-Pasha solar cells by ECN in WP5. Furthermore Al2O3: B2O3 layers (CLS) have been optimized and applied at the rear side of c-Si solar cells been by ECN in WP5.
- Different methods to fabricate ultrathin SiO2 layers have been investigated. Based on the wet-chemical deposition approach ultrathin SiO_2 (0.8nm) passivation, tunneling layers have been developed. It has been shown, using cell precursor structures as well as finalized solar cells, that high effective lifetimes of 1ms can be reached and that it can be beneficial to substitute the (i)a-Si:H buffer layer in a solar cell by a SiOx tunnel layer at the front side of the cell. An unexpected additional benefit of this layer is the improved band bending and thus current collection efficiency and fill factor. This benefit is only present if the (i)a-Si:H layer is substituted in the p/n junction on (n)c-Si substrates. An overall improvement of the cell efficiency by ~0.3% abs. could be shown, albeit on a generally very low level of cell performance.
- A nanolayer with nanodots based on Si-NDs in SiO2 has been developed and high transmittance and effective doping as well as electrical conductivity have been realized. Therefore this layer could be applied as an emitter in thin film poly-Si solar cells. Although important progress has been made and fundamental scientific questions have been addressed this approach seems not suitable for application to solar cells with increased efficiency within the short time period left in the project.
- It has been shown that Si and/or Ge nanoparticles embedded in Si oxide, nitride and carbide matrix in the form of superstructure can be fabricated by magnetron sputtering. It is also shown that a very good control of the average diameter can be obtained by preselecting the desired thickness of the corresponding layer. Although important progress has been made and fundamental scientific questions have been addressed this approach seems not suitable for application to solar cells with increased efficiency within the short time period left in the project.
- SiO_2/SiO multilayer were deposited by e-beam and subsequently annealed at high temperature in order to form Si nanocrystals embedded in a thin SiO_2 matrix. The resulting nanostructures were characterized using electro-optical techniques in order to text the electrical response of the system to monochromatic light.
- Atomic Layer Deposition (ALD) Al_2O_3 layers were developed with excellent passivating properties when processed at low temperatures. The integration of the ALD-Al_2O_3 films in silicon based solar cells revealed that, under higher temperature processing, their performance deteriorates. Extensive investigation of the chemical-structural evolution of the Al_2O_3 film was performed to identify the origin of lifetime deterioration upon high temperature annealing.

- SiO_2 layers were grown on Si substrates by ALD at low temperature and their passivating properties were investigated. Lifetime measurements revealed these films provide a limited passivation effect. The results were supported by electrical characterization of the resulting SiO_2/Si interface in terms of density of fixed charges and of interface states.
- Comprehensive morphological and structural characterization of Au deposition on SiO_2 and HfO_2 was performed and the final characteristics of the Au nanoparticle population were investigated as a function of the deposition conditions and subsequent thermal treatment.
- ~15% conversion efficiency by implementation of ultra-thin Al_2O_3 passivation tunnel layer between AZO and a-Si:H emitter for n-type epi-Si(30 μm)/n+ Si substrate solar cell structure has been achieved.

ELECTRICAL, OPTICAL AND STRUCTURAL PROPERTIES OF INDIVIDUAL NANOMATERIALS AND RELATED SOLAR CELL STRUCTURES

Work on this topic was part of WP4. In this WP, analysis of composition, electrical, optical and structural properties of the nanostructures, layers and solar cell structures supported by *ab initio* simulations in some cases have been done.

Analysis and characterization of composition and electrical properties of individual nanolayers and related solar cell structures

Characterization of Si/TiO2:AuNPs, Si/SiO_2 and Al_2O_3 interfaces was implemented by HF-CV experiments. Formation of defects at the interface between Si and different crystalline SiO_2 polymorphs upon thermal treatment was explored in the force field approach. For quantitative assessment of an influence of nanostructured layers deposited on top of silicon wafer, the photoconductivity method is developed and used to evaluate the EQE and IQE characteristics of Si substrates covered by these nanostructured layers. SPV method was used to determine band bending of various nanolayers and nanolayers with nanoparticles. Voltage-dependent SPV method was used to determine interface defect densities of SiO2 passivation layers. The electrical properties of chemically deposited thin films of $(Al_2O_3)_x(B_2O_3)_{1-x}$ with dispersed Si nanoparticles (20 nm) have been studied. The transverse conductivity and the sheet resistance have been evaluated, when different types of substrates are used.

Characterisation techniques used for developing an amorphous silicon emitter on nanotextured black silicon surfaces

The development of a silicon heterojunction solar cell with a hydrogenated amorphous silicon emitter layer on top of a nanotextured “black” silicon surface poses high challenges and thus during optimization different characterisation techniques, such as scanning electron microscopy (SEM), field-dependent surface photovoltage (SPV), lateral conductivity measurements, spectroscopy and quantum efficiency (QE) measurements in the UV and visible range as well as simulation based analysis of QE measurements. Simulations have been performed with using the AFORS-HET solar cell simulator and a simple optical model.

Optical analysis and characterization of individual nanomaterials and related solar cell structures

PL method was applied to investigate quantum size effects and to determine the photogenerated minority charge carrier lifetime in Si nanodots.

Optical transmission and reflectance of various nanomaterials such as ITO nanorods, plasmonic particles were measured.
The optical characteristics (transmittance and reflectance) have been studied for nanolaminate structures with TiO_2 depending on film thickness of the individual layers and of the density of the metal granules. The ratio between the transmittance and reflectance is analyzed in order to detect the absorbance. The aim is to find out optimal conditions for decreasing the reflectance in the infrared spectral region.
The optical properties of the chemically deposited $(Al_2O_3)_x(B_2O_3)_{1-x}$ with dispersed Si nanoparticles (20 nm) films are studied as a function of the thermal treatments.

Structural and chemical characterization of nanomaterials and interfaces

NPs and NWs containing structures produced by sevreal nanoPV partners have been characterized by SEM, AFM, XPS, Raman, FTIR. In some cases, ab-initio simulations for advanced electronic structures using DFT approach have been done. **Fig. 18** shows that thin Si NW (labeled as "mini", 1.2 nm in diameter) privide formation of a direct band gap structure. The cross-over for a transition between in-direct and direct Si Nws structures is in the range of ~5 nm ("full") for the NW diameter.

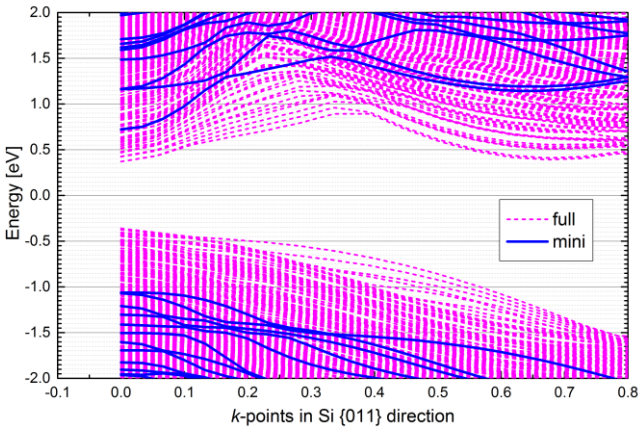


Fig 18: Electronic structure of Si NWs with different diameters: "mini" – 1.2 nm; "full" – 5 nm.

Characterization and testing of solar cells containing nanomaterials

A special workstation is designed for measuring I-V characteristics for small solar cells with micromanipulator for small contact areas. The illumination intensity is calibrated of 100mW/cm^2. The measuring conditions are programmed and the results are recorded in digital form. I-V characteristics are measured sequentially in the dark and lighting. Measurement of I-V characteristics of HIT and SHJ solar cells before and after deposition of ZnO NWs by electrochemical method and of the structure n-type c-Si/p+ NP Si (deposited by magnetron sputtering and annealing); were made. IV, Suns-Voc, and EQE characterization of nanowire-based solar cells was performed. This applies to nanowires prepared on silicon wafers and on polycrystalline silicon thin films deposited on glass, with axial as well as with radial pn-junction. Spatially resolved EQE measurements were performed by light beam induced current (LBIC) to give local information on nanowire based solar cells prepared on polycrystalline silicon deposited on glass.

Conclusions

Significant results of WP4 activities can be summarised as follows:

- It has been shown (PL) that a band gap narrowing is possible by adjusting the nanodot size and thus the absorbance can in principle be adjusted by band gap engineering. However an efficiency increase

of solar cells by exploiting this effect is still far from realization, in particular because of low passivation quality of Si nanodot surfaces**.**

- Optical experiments show that ZnO NW layers can be deposited on the surface of different solar cells - on poly-Si wafers, HIT structure by electrochemical method. The films demonstrate antireflection properties. The optimisation of the conditions of growing has to be optimised to avoid creation of damages around the grid contacts of HIT solar cells. ZnO NW films are deposited on the surface of steak structures glass/Ag/ZnO:Al/Ag/ZnO:Al with plasmonic properties. These structures can be applied as a back reflector with higher diffused reflection properties and increased effective area for this films solar cells deposition.
- Interface between silicon and its oxide has been investigated theoretically using molecular dynamics based on relax force field. It is shown shown that low efficiency of Si nanocrystal solar cells may be a result of the difference in the structural relaxation in Si and SiO2 prior and during annealing that leads to stress formation in Si lattice due to presence of the interface.
- Spatially resolved EQE measurements were performed by light beam induced current (LBIC) to give local information on nanowire based solar cells prepared on polycrystalline silicon deposited on glass. It has been demonstrated, that the EQE of these cells is rather homogeneous varying by about 10% on the cell area that is acceptable for further scaling the method of nanowire based solar cells preparation.
- It is shown that at the ITO/Si interface in Si based heterojunction solar cell structures, formation of Indium based local conductive channels as well as thin SiOx layer occurs.

DESIGN, PROCESSING, CHARACTERIZATION AND TESTING OF SOLAR CELLS AND MODULES

Work on this topic was part of WP5. This WP has the following objectives:

- Selection of 3-5 most promising nano-materials (particles and layers) for proof of concept demonstration on wafer-based silicon solar cells and/or modules (all partners); This selection will be made from the broad range of different activities, i.e. advanced nanotechnology based emitters, BSF & local contacts, advanced passivation and antireflection layers, implementation of MEG as well as up- and down conversion effects.
- Selection of 3-5 most promising nano-materials (particles and layers) for proof of concept demonstration on thin-film silicon solar cells and/or modules (all partners). This selection will be made from the same range of activities as indicated above for wafer-based silicon solar cells.
- Selection of 2-3 most promising NRs/NWs based technologies for advanced cell structures.
- Development of cost effective application of nanomaterials to solar cells and modules. The proof of concept with respect to industrial processes and efficiency gain will be demonstrated in this WP (proof of concept means: proof of the technology on tens of cells).

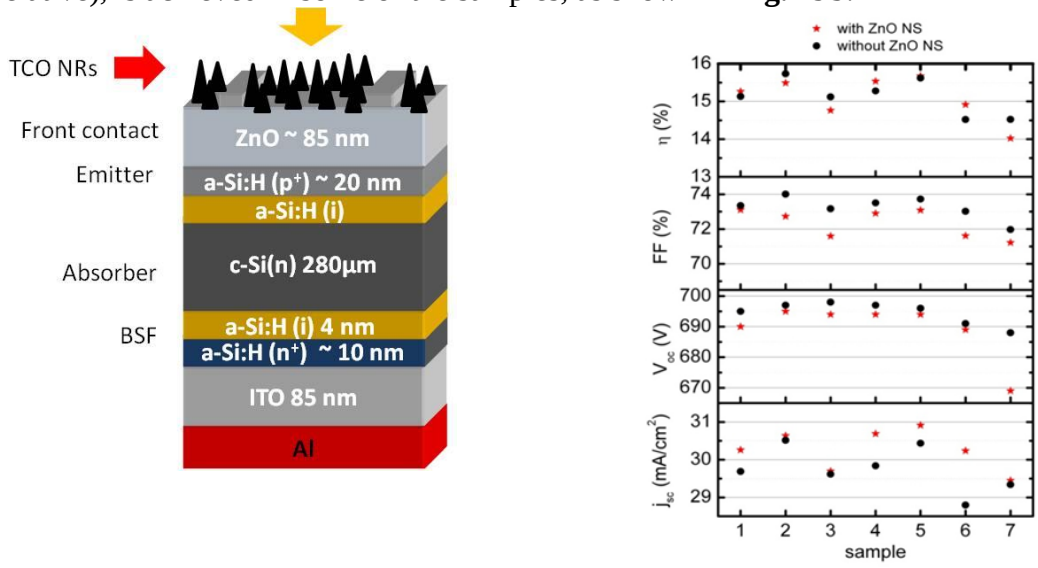
Based on the results of the material investigations, 9 materials were implemented in wafer-based Si cells, and 11 materials were implemented in thin-film Si cells. Based on these results the most promising concepts have been selected for further optimization, leading to efficiency enhancement in 5 cases within the wafer-based Si concepts, and 3 cases within the thin-film Si concepts.

Solar cell results (selected cases)

The results for the implementation of nanomaterials in solar cell structures, leading to efficiency enhancement (selected cases), are shown below.

ZnO nanowires for SHJ solar cells

The solar cells have a structures: Ag grid/ITO/(p)a-Si:H/(i)a-Si:H/(n)c-Si/(i)a-Si:H/(n+)a-Si:H/Al (see **Fig. 19a**). The current-voltage characteristics of the samples before and after deposition of ZnO NS array films on the top side of the SHJ solar cells were evaluated. It is seen that after implementation of the ZnO NS array films, a few percent relative increase in short circuit current, J_{sc}, and efficiency, η (up to 2.7% relative), is achieved in some of the samples, as shown in **Fig. 19b**.



a) b)

Fig. 19 Implementation of TCO nanorods in SHJ solar cells: a) schematic drawing of TCO nanorods integration (note that in final design, the ZnO front contact was replaced by ITO, b) *I-V* parameters of SHJ cells before and after ZnO nanorods application.

Black silicon nanotexture for bifacial solar cells

Bifacial solar cells on n-type material were prepared with standard random pyramid texture for the reference cell, and with black silicon nanotexture on the front side to enhance the performance, as described in **Table 1**. The cell results are summarized in **Table 2**.

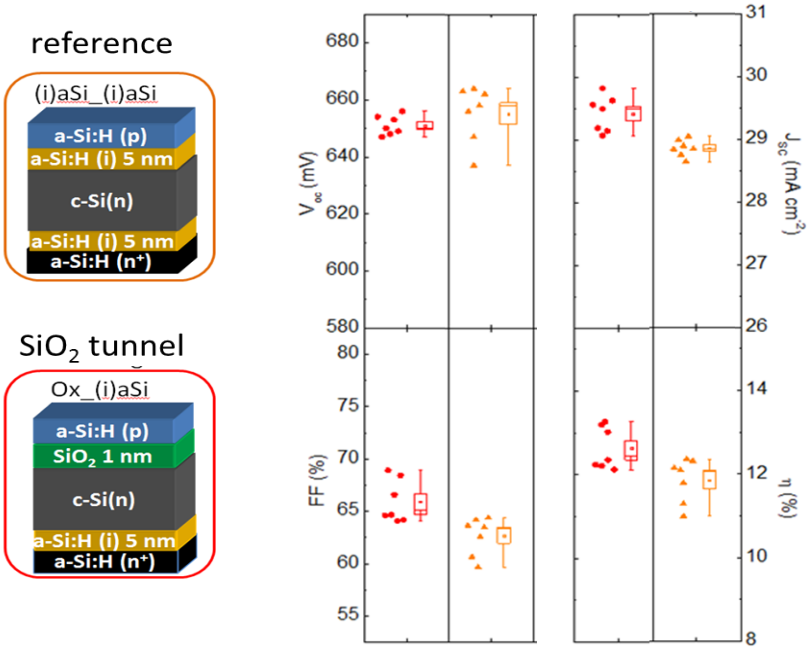
Table 1 Description of sample configuration with black silicon etching (2.5x2.5 cm^2)

Description	Sample	Comments
grids/ITO/p^+nn^+/IFO/grids reference redistributed diffused profiles, annealing in N2, 1000°C, 1h 30'	reference	Normal pyramid textured front p-side & Normal pyramid textured rear n-side, reference cell
p^+nn^+/ p-side black, redistributed diffused profiles	Black Si	Black front p-side & Normal pyramid textured rear n-side

Table 2 Solar cell results with black Si nanotexture on the front, compared to reference

	reference	Black Si
pseudo-*FF* [%]	**67.9**	**75.6**
J_{sc} [mA/cm^2]	**30.7**	**33.0**
V_{oc} [mV]	**572**	**576**
***FF* [%]**	**65.3**	**68.6**
***Efficiency* [%]**	**11.5**	**13.0**

SiO_2 tunnelling passivating layer

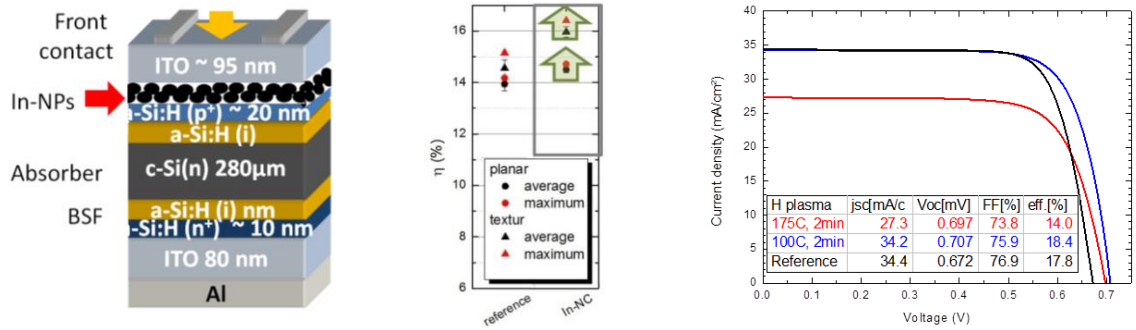


The SiO_2 tunneling buffer layer is replacing the a-Si:H(i) layer on the front. A reference with a-Si:H(i) layers was processed as well. From the cell results, presented in **Fig 20**, it is clear that replacing the front side a-Si:H(i) layer with a SiO_2 tunneling buffer layer yields improved results. An efficiency gain of about 0.5% absolute is observed for this configuration compared to the reference, on a level of 13% efficiency.

Fig. 20 Silicon heterojunction reference solar cell and with a SiO_2 passivating tunneling layer on the front.

In-NPs for TCO/a-Si:H/Si

In silicon heterojunction solar cells, emitters with In-NP integrated are compared to reference cells (**Fig. 21**).For both planar and textured cells, the integration of In-NP at the front leads to an increase of efficiency, due to increase in both J_{sc} and V_{oc}.



a) b) c)

Figure 21: Silicon heterojunction solar cell with In-NP at the emitter/contact interface: a) schematic cross-section, b) efficiency plots of run 1, c) IV curves and IV parameters after optimization of the H-plasma treatment

For this approach In-NPs were processed by a H-plasma induced reduction of an ultrathin ITO layer with a thickness of 5 to 10 nm at OIPT. As substrate n-type wafers with a planar (100) surface and with an alkaline etched, random pyramid texture have been used. A conventional a-Si:H emitter stack based on ultrathin layers and additionally a 5 to 10 nm thin ITO layer has been deposited. Afterwards, plasma processing was done at 100°C for 2 min. To finalize the solar cell an a-Si:H back surface field layer stack as well as ITO layers at front and back side to optimize optics and contacting, have been deposited. An improved efficiency as compared to the reference of 0.6% absolute in efficiency can be observed for the solar cell with In-NPs processed at 100°C. Maximum efficiencies of 18.4% have been reached and thus we can recommend this approach for improved silicon heterojunction solar cell design.

a-Si:H emitter nanolayer for SHJ cells

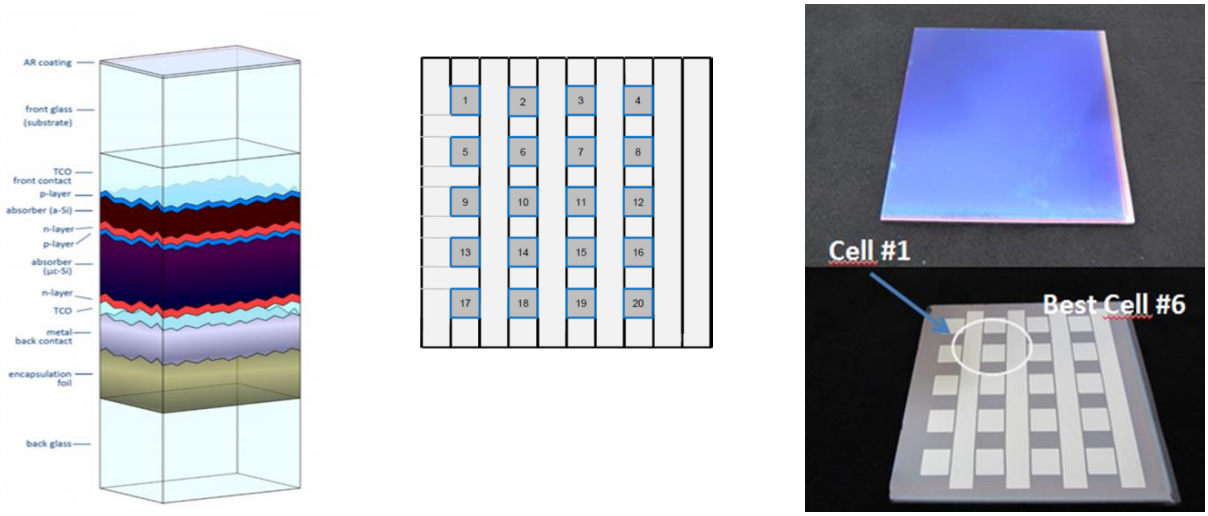
In silicon heterojunction solar cells, the a-Si:H emitter was optimized for enhanced performance. Background knowledge from ECN was brought in to present the optimization of deposition parameters and thickness of the emitter nanolayer. The implementation of this optimized nanolayer led to an efficiency increase of 0.6% absolute, at the level of 19.8% (20.2% best) cell efficiency. In **Table 3** the cell parameters are listed for the reference emitter (1), after deposition parameter optimization (2) and thickness optimization (3).

Table 3 Median (best) *I-V* parameters of the SHJ cells of 156x156 mm^2 size with emitter nanolayer.

	Emitter 1	Emitter 2	Emitter 3
J_{sc} [$mAcm^{-2}$]	35.8	36.0	35.9
V_{oc} [V]	0.721	0.724	0.726
FF [-]	0.744	0.757	0.760
efficiency	19.2% (19.5%)	19.7% (19.9%)	19.8% (20.2%)

Ag NP plasmonic nanostructures for thin-film Si tandem cell

Plasmonic silver nanoparticles (Ag NP) have been introduced at the back side of thin film solar cells. To implement the Ag NP layer on larger area and for solar cells processed with industrial equipment, a-Si:H/µc-Si thin film tandem solar cells have been prepared, as sketched in **Fig. 22**.



a) b) (c)

Fig. 22 a) a-Si:H/ µc-Si tandem solar cell, a-Si:H/µc-Si absorber on glass b) schematic layout of the cells on a wafer, c) after deposition of Ag nanostructures and AZO deposition, and after contact structuring.

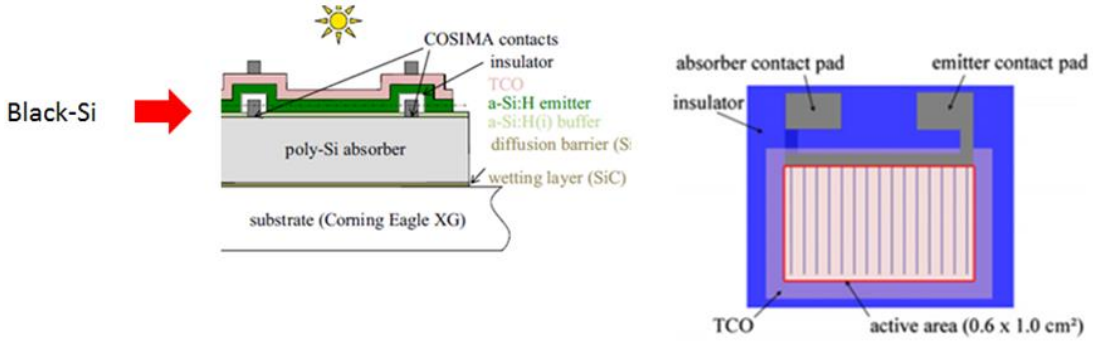
Table 4 Photovoltaic parameters of the best thin film Si solar cells with plasmonic layer, as compared with the reference (without back reflector).

sample	Jsc	Voc	FF	eta
Ag NP by ESAVD	13.81	937	75.5	9.8%
Reference	13.98	917	74.0	9.5%

The presence of Ag nanoparticulate (NPs) layer by ESAVD has increased the thin film Si solar cell efficiency by 0.3% absolute to 9.8% as compared with the reference solar cell without the Ag nanoparticulate layer (9.5%), as listed in **Table 4**.

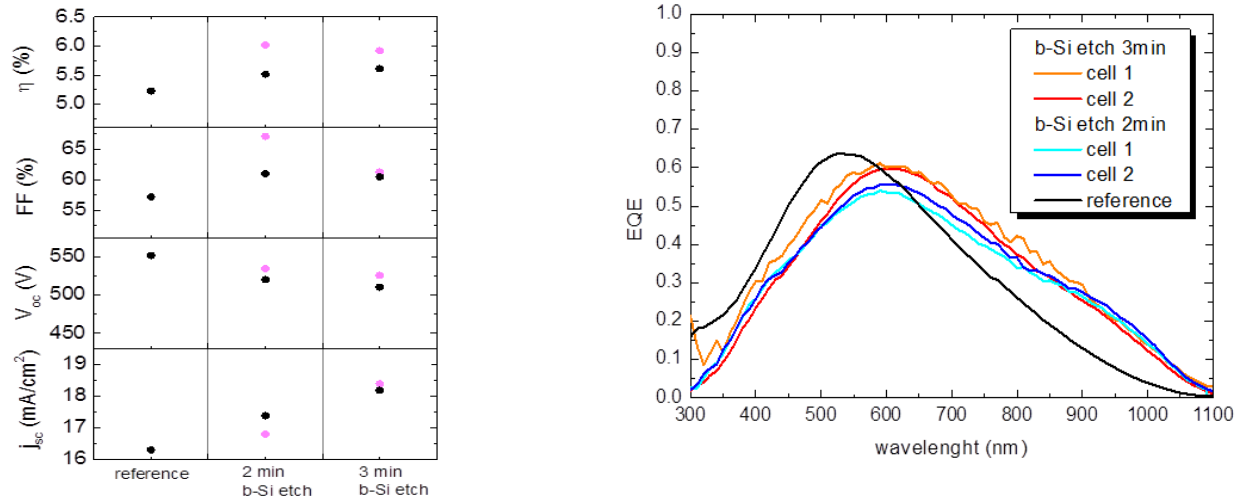
Black nanotexture for thin-film FrontERA cell

Cells have been prepared on 5x5 cm^2 substrates using the advanced FrontERA contacting scheme (see **Fig. 23**). Because shallow texture is of advantage in terms of passivation while a deep texture is of advantage in terms of anti-reflection properties, samples with two different b-Si etching times (2 min and 3 min) have been prepared. From the results, presented in **Fig. 24**, it can be concluded that black Si is well suited as a texture for thin film solar cells. The average efficiency increase is >5% relative for the nanotexture compared to the reference.



a) b)

Fig. 23 FrontERA contact system for contacting poly-Si thin film solar cells with b-Si texture

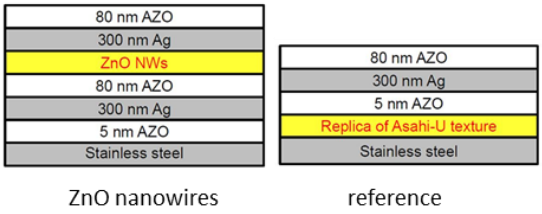


a) b)

Fig. 24 Solar cell parameters (a) and external QE (b) for 10x6 mm^2 solar cells on a 5x5 cm^2 substrate with a poly-Si thin film absorber and a black-Si texture with different texture depth. In (a) the black dots indicate the average value and the pink dots the solar cell with the maximum efficiency. In (b) the external QE measurement two cells for each MCE time are shown to provide prove of the reproducibility.

ZnO nanowires for thin-film nip cells

ZnO nanowires were integrated at the rear side of the cells, for rear side scattering purposes. For ensuring good contact to the cell, it was necessary to deposit the back contact on top of the ZnO nanowires (Fig. 30, top). This leads to an efficiency gain of 0.7% absolute compared to the reference cell, as shown in **Fig. 25** (bottom).



Sample	Texture	V_{oc} (mV)	J_{sc} (mA/cm²)	FF	Eff.	
DPC2-368-NWsBC	ZnO NWs/Ag/AZO	850	13.8	0.621	7.28%	
DPC2-368-CBR	Replica of Asahi-U texture	851	12.4	0.622	6.56%	(reference)

Fig. 25 ZnO nanowires integrated at the rear in thin-film nip cells (top). For simplicity only the substrate with back contact is sketched; on top of this the cell is deposited. Cell results (bottom) are given for the ZnO nanowires cell and the reference.

Conclusions

Significant results of WP5 activities can be summarised as follows:

Wafer-based silicon solar cells: (i) efficiency gains for ZnO nanowires, black silicon nanotexture, SiO_2 tunneling passivating layer, In-NP contacting layer (18.4%) and a-Si:H emitter layer (20.2%); (ii) highlights for Al_2O_3 (V_{oc} gain); successful integration of black silicon in SHJ (17.2%) and Al_2O_3/B_2O_3 in p-Pasha (17.0%).

Thin-film silicon solar cells: (i)efficiency gains for Ag NP plasmonic nanostructures, black silicon nanotexture and ZnO nanowires; (ii) highlights for Ag/AO/Ag/AZO plasmonics (high Isc gain), nanotextured Al (7.7%), epi-Si cells with a-Si:H emitter (12.6%), epi-Si cells with Al2O3+ a-Si:H emitter (15.2%), epi-Si cells with ITO (14.0%).

Nanomaterial (Si NWs) based solar cells: (i) Si NWs based solar cells with radial a-Si hetero-emitter etched into wafer: 10.0% efficiency; (ii) fabrication of Si NW solar cells on larger (50x50 mm^2) substrates.

Summary of efficiency gains obtained by implementation of nanomaterials

Si wafer-based cells: (i) ZnO nanowires for antireflection coating: 2.7% relative; (ii) Black silicon nanotexture: 1.5% absolute; (iii) SiO2 tunneling passivating layer: 0.5% absolute; (iv) In-NPs contacting layer: 0.6% absolute; (v) a-Si:H emitter layer: 0.6% absolute (enhanced to >20% efficiency).
Thin film silicon cells: (i) Ag NP plasmonic nanostructures: 0.3% absolute; (ii) Black silicon nanotexture: >5% relative; (iii) ZnO nanowires for antireflection coating: 0.7% absolute.

ASSESSMENT OF TRASFERABILITY TO INDUSTRIAL PRODUCTION

Work on this topic was part of WP6. The main goal of this work package is to prove the viability of some selected new technologies developed by the nanoPV Consortium for the processing of Si based solar cells on industrial equipment (lead by ECN). The selected process chains for cost-effective processing of Si based solar cells and related solar cell modules have been tested regarding a feasibility to transfer such chains to production equipment. Based on the results from the fabrication of solar cells and modules on laboratory scale (WP 5) the advantage of the proposed advanced technologies has been evaluated and demonstrated for some selected cases. This WP has the following objective: Transfer of the selected solar cell and solar cell modules processing chain to production equipment.

Transferability to industrial equipment

Concepts for processing equipment chains have been defined for three cell concepts with integrated nanomaterials that were assessed for transferability to industrial equipment. The n-Pasha concept with Al_2O_3 passivating nanolayer at the rear and the silicon heterojunction cell with a-Si:H (emitter) nanolayers can be completely processed on industrial equipment. The p-Pasha concept with Al_2O_3/B_2O_3 passivating nanolayer at the rear can be largely processed on industrial equipment; the transfer to industrial equipment of the Al_2O_3/B_2O_3 application is not proposed here, but not seen as a large risk for the transfer of the process to industrial equipment. Processing equipment on industrial level for manufacturing of completely nano-based solar cells (route 2) is proposed.

Conclusions

Wafer-based silicon solar cells have been manufactured on industrial equipment, achieving high efficiencies of over 20%. Three solar cell types have been manufactured in several cell runs. These three concepts are:

- n-Pasha solar cell with thin Al_2O_3 passivating nanolayer: in this project, the efficiency was on same level as the reference without Al_2O_3 nanolayer; potential improvement was identified.
- Silicon heterojunction solar cell with a-Si:H nanolayers: 20.2% efficiency achieved; efficiency increase of 0.6% absolute by optimized emitter nanolayer.
- p-Pasha solar cell with an Al_2O_3/B_2O_3 passivating nanolayer: successful integration of Al_2O_3/B_2O_3 passivating layer; more research is needed to implement this material successfully.