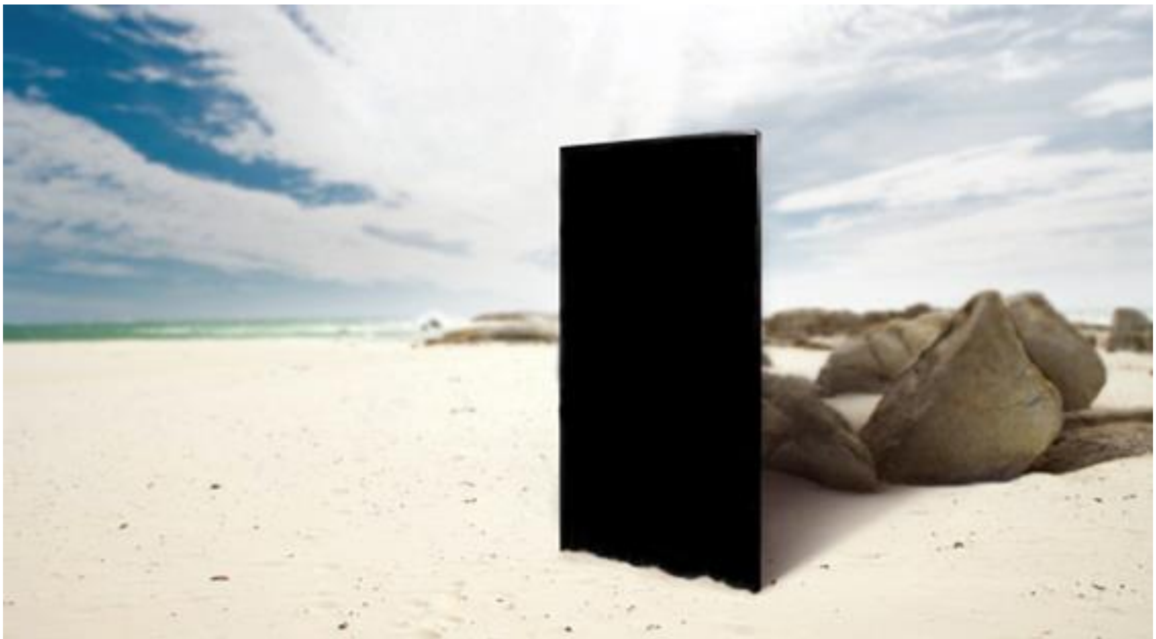
FINAL REPORT

EUDP 64015-0006

BLACK SILICON BIPV – PHASE 1

Cost and energy effective all-black solar cell panel



WRITTEN BY

Peter Behrensdorff Poulsen, Sune Thorsteinsson, DTU Fotonik

Rasmus Schmidt Davidsen, Ole Hansen, DTU Nanotech

Peter Torben Tang, Io Mizushima, IPU

Jesper Frausig, Gaia Solar

Final report

1.1 Project details

Project title	Cost and energy effective all-black solar cell panel | Black Si BIPV | Phase 1
Project identification (program abbrev. and file)	Jnr. 64015-0006
Name of the programme which has funded the project	EUDP
Project managing company/institution (name and address)	DTU Fotonik, Frederiksborgvej 399, 4000 Roskilde Peter Behrensdorff Poulsen, ppou@fotonik.dtu.dk
Project partners	DTU Nanotech IPU Gaia Solar
CVR (central business register)	DK 30 06 09 46
Date for submission	September 30th 2016

1.2 Short description of project objective and results

English

The project is a 1-year proof-of-concept & proof-of-business project. Methods for creating modules with black silicon cells and black front grid has been developed and a few prototype modules of low quality fabricated and used for probing the market interest for the all black silicon technology. Furthermore, the superior angular light absorption on the module level has been verified.

The project has fallen in the following work packages (WP).

- WP 1 Project Management
- WP 2 Investigation of interconnection method
- WP 3 Investigation/proof-of-concept of black electroplating methods to make the ribbons black
- WP 4 Design and production of Black Silicon cells
- WP 5 Investigation of module technology supporting the all black silicon cell, proof-of-concept production and module characterization.
- WP 6 Proof-of-Business of Black Silicon BIPV

This project is precursor to EUDP 64016-0030 addressing cost efficient production, reliability, scaling up and the commercialization starting October 1st 2016.

Dansk

Projektet er et 1-års proof-of-concept & proof-of-business projekt. Metoder til at skabe moduler med Black Silicon celler med sorte loddetabs er blevet udviklet og et par prototype-moduler af lav kvalitet fremstillet. Sidstnævnte er anvendt til propning af interessen i markedet for den kommercielle udgave af den udviklede teknologi. Endvidere er den overlegne vinkelafhængige lysabsorption af black silicon på modulniveau blevet bekræftet.

Projektet er realiseret gennem de følgende arbejdspakker (WP).

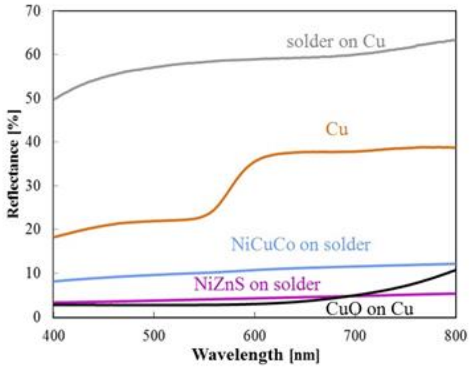
- WP 1 Projektledelse
- WP 2 Undersøgelse opstrengningsmetode
- WP 3 Undersøgelse/proof-of-concept af sorte strenge via elektrokemisk behandling.
- WP 4 Design og produktion af Black Silicon celler
- WP 5 Undersøgelse af om modulteknologien understøtter black silicon cellen og de sorte strenge samt proof-of-concept produktion og modulkarakterisering.
- WP 6 Proof-of-Business at Black Silicon BIPV

Dette projekt er forløber for EUDP 64016-0030 der adresserer omkostningseffektiv produktion, pålidelighed, opskalering og kommercialisering startende 1. oktober 2016.

1.3 Executive summary

The project has successfully solved the objectives and shown both proof-of-concept and proof-of-business of an all-black solar panel based on black silicon and black strings. Several electrochemical methods have been pursued to make the strings black and though not perfect the reflectance has been lowered significantly by more than a factor 10. Some approaches are better than others to achieve low reflectance. Especially NiZnS, NiCuCo and CuO have been pursued.

In summary, Cu ribbons strings with CuO is the best match for black silicon with respect to the all-black appearance, because of the comparatively low reflectance but reacts with the laminate and form gas bubbles. So some optimization is still to be done, but the time to up-scaling is not far away.



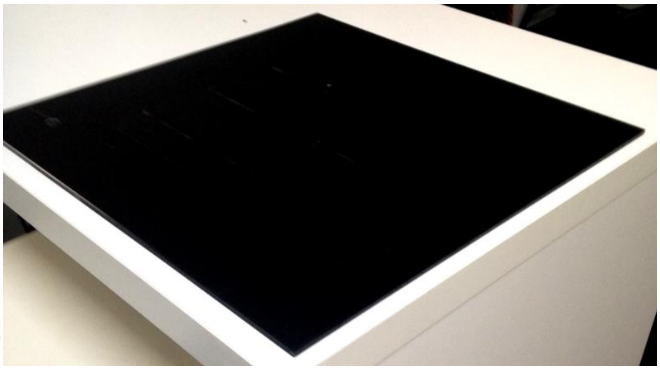


Figure 1 – Left, Measured reflectance as function of wavelength of interconnecting ribbons without (bare Cu, and Cu with solder) and with (NiCuCo, NiZnS, and CuO) black coatings. Right, Photo of all-black prototype of black silicon cells with treated inter-connected ribbons.

Black silicon cells has been produced and implemented in prototype panels and the most successful one is shown in Figure 1 to the right. The dissemination processes has led to high both scientific and commercial interest. On the latter Meyer Burger (producers of process equipment for solar cell production lines) has contacted the project group with specific interest in having their process equipment tuned/developed to be able to produce black silicon and deliver process equipment being able to integrate such a process industrially. Furthermore, other panel producers are interested in being able to produce the black silicon panels.

This gives several business opportunities to follow for the project group which will be pursued in the phase 2 project (EUDP 64016-0030).

1.4 Project objectives

As described above project is a 1-year proof-of-concept & proof-of-business project. The objectives is to develop methods for creating modules with black silicon cells and black front grid and a few prototype modules of low quality should be fabricated and used for probing the market interest for the all black silicon technology. Furthermore, the superior angular light absorption on the module level has been verified.

The project has fallen in the following work packages (WP).

- WP 1 Project Management
- WP 2 Investigation of interconnection method
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The project evolved perfectly as planned and the objectives was all meet with great success. The risks in the project were pretty high so the project group is very happy with the achievements. If by luck or due to strong competences is not clear, but even the first proto-type with black strings was pretty successful both in appearance and functionality – see Fig-ure 2. Several electrochemical treatments were explored and most of them seemed compati-ble with the lamination process. Of course the best one in appearance made bubbles in the laminate, so there is still some optimization to be done, but proof-of-concept was definitely proven and the probing of the market shown an ever increasing demand for the concept which will be developed further and commercialized in EUDP 64016-0030 Black Silicon BIPV - Phase 2.

Figure 2 – first prototype of an all-black PV module (right) with an identical reference module (left) fabricated identical with the standard process.

1.5 Project results and dissemination of results

In general, the overall goal of the project has been obtained, since all-black Si solar panels have been successfully produced using conventional front-contacted (screen-printed) Si solar cells. The cells are textured by the unique 'black silicon' process and interconnected by several differently coated black ribbons. The combination of black Si and black ribbons results in an aesthetic, all black appearance and the electrical results confirm that black ribbons work acceptably well at interconnecting. Adhesive glue and soldering were tested and compared. It seems that soldering CuO-coated ribbons would be an ideal solution. Neither cell performance, nor interconnection method has been fully optimized, but these preliminary results are encouraging and future work will be focused on solving the presented issues and scaling the concept to larger panels.

<u>Black Silicon</u>

Black silicon was realized on 156x156 mm^2 Czochralski (CZ) mono-crystalline Si wafers by mask-less reactive ion etching (RIE) in SF_6 and O_2 plasma at room temperature. Figure 3 shows a scanning electron microscope (SEM) image of the resulting nanostructure topology. The nanostructure topology consists of conical-like hillocks with average height of 300 nm and average spacing of 300 nm.

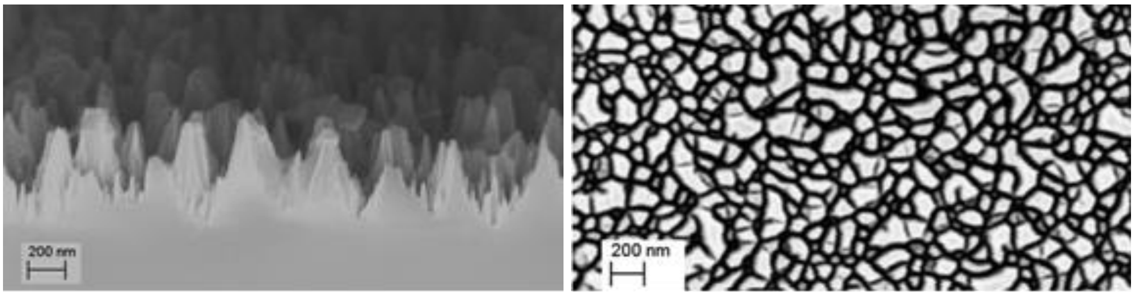

Figure 3: Scanning electron microscope image at 40 degrees (left) and 0 degrees tilt (right) of the nanostructure topology resulting from mask-less reactive ion etching.

Normal incidence reflectance measurements of the RIE-textured Si surfaces were performed using a broadband light source (Mikropack DH-2000), an integrating sphere (Mikropack ISP-30-6-R), and a spectrometer (Ocean Optics QE65000, 300-1000 nm).

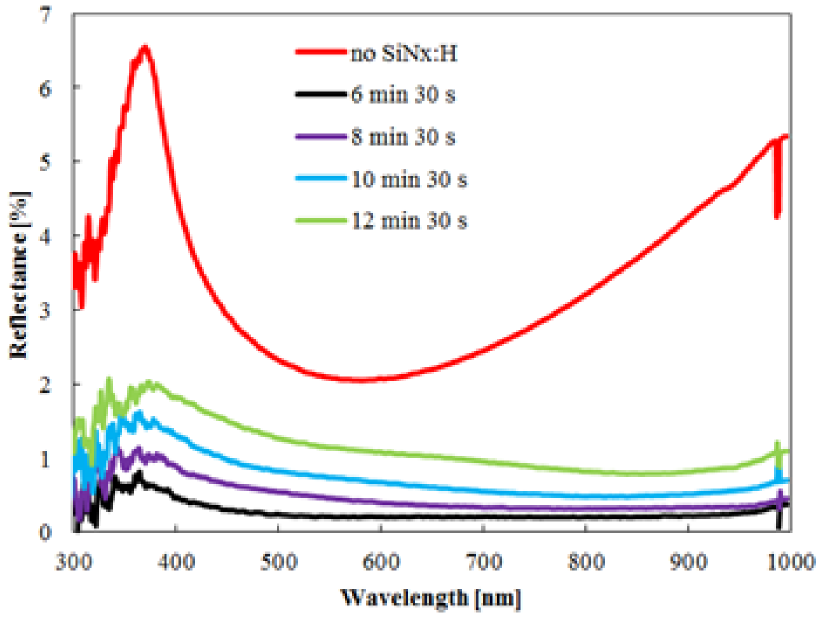

Figure 4: Measured total (diffuse+specular) reflectance of black Si with SiN_x:H AR-coating as a function of wavelength in the range 300-1000 nm for four different PECVD SiN_x:H deposition times representing four different SiN_x:H thicknesses.

For the reflectance measurements hydrogenated silicon nitride (SiN_x:H) deposited by plasma-enhanced chemical vapor deposition (PECVD) was applied. An n^+ emitter was formed on the RIE-textured Si using $POCl_3$ as dopant source prior to the deposition of SiN_x:H. Since the refractive index profile of black Si is fundamentally different from that of conventionally textured or planar Si, the optimal SiN_x:H thickness for black Si was investigated. The deposition time of the PECVD process was varied in steps of 2 minutes from the 'standard' time of 6 min and 30 s to 12 min and 30 s. The reflectance was then measured for the different SiN_x:H thicknesses on RIE-textured Si wafers. The result is shown in Figure 4 which shows that a PECVD process time of 6 min and 30 s minimizes the reflectance of black Si. In general SiN_x:H AR-coating reduces the reflectance of black Si. Deposition times are stated instead of SiN_x:H thicknesses, since the exact thickness on black Si is not fully known due to the complicated surface morphology. On conventionally textured Si a 6 min and 30 s deposition yields a SiN_x:H thickness of ~ 60 nm. Due to the broadband anti-reflective properties of black Si the SiN_x:H thickness does not need to be optimized in terms of minimized reflectance at a certain wavelength. It seems from Figure 4 that the reflectance increases monotonically with SiN_x:H thickness in the thickness range investigated.

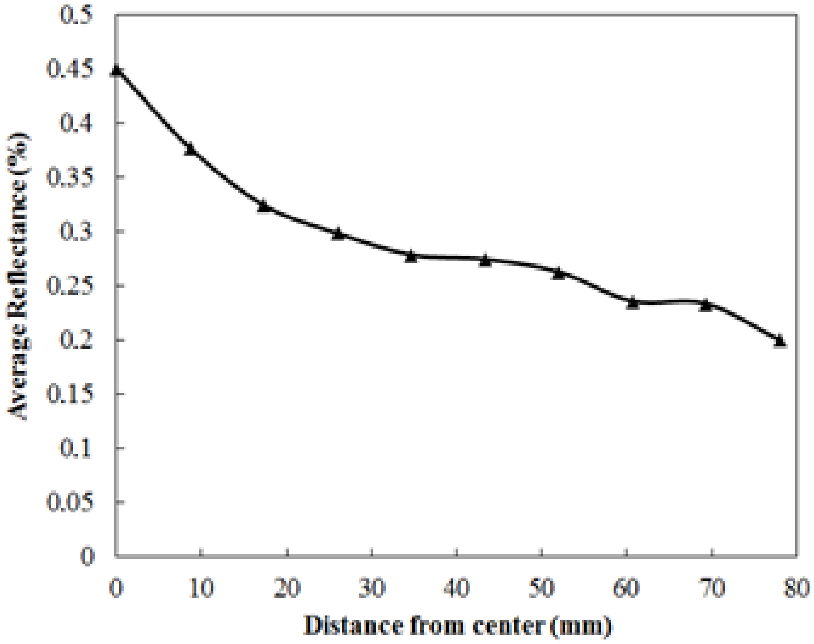

Figure 5: Measured total (diffuse + specular) reflectance of RIE-textured Si with SiN_x:H averaged over the wavelength range 300-1000 nm as function of the distance from the center of a 156x156 mm^2 CZ wafer.

In order to quantify the spatial uniformity of RIE-texturing, the reflectance was measured at different positions across a 156x156 mm^2 CZ wafer textured by mask-less RIE after $POCl_3$ emitter diffusion and PECVD of SiN_x:H (6 min and 30 s). The total (diffuse + specular) reflectance was measured in the wavelength range 300-1000 nm and the integrated average reflectance is plotted as function of distance from the wafer center in Figure 5. Figure 5 shows that the integrated average reflectance is below 0.5% across the entire 156x156 mm^2 wafer. The average reflectance decreases towards the edge of the wafer, but even though the relative difference from center to edge is significant, the absolute difference is ~ 0.2%. The deviation in reflectance across the wafer is probably due to the plasma chamber and wafer geometry.

Solar Cell processing

Solar cells were fabricated from 156x156 mm^2 p-type CZ Si wafers using the following process steps:

1. Saw damage removal using an HF:HNO_3:CH_3COOH etchant mixture
2. Maskless RIE texturing
3. Diffusion of n-type emitter in a tube furnace using a $POCl_3$ source to obtain a sheet resistance of ~120 Ω/sq.
4. Deposition of anti-reflection coating on the front surface by plasma enhanced chemical vapour deposition (PECVD)
5. Screen-printing and firing of metal contacts
6. Laser edge isolation

The formation of an n-type emitter, using $POCl_3$ as the phosphorous doping source, was carried out using a Tempress TS-8603 tube furnace at a temperature of 836-838 ºC for 37 minutes, followed by a 10 minutes drive-in. Hydrogenated amorphous silicon nitride (a-SiN_x:H) was deposited using an Oxford Instruments PlasmaLab System133 PECVD tool with silane, ammonia and nitrogen at a temperature of 400 °C and a pressure of 800 mTorr for 6 minutes and 30 seconds. For the contact formation, an EKRA X5-STS semi-automatic screen printing machine was used. The contacts were printed using Ag paste (DuPont PV18A) on the front and Al paste (Monocrystal PASE-1207) on the rear. The contacted cells were subsequently dried and co-fired in a belt furnace with temperatures in the range of 780-945°C and a belt speed of 520 cm/min. Edge isolation was performed by laser ablation using a J-1030-

515-343 FS System from Oxford Lasers. A wavelength of 515 nm and a repetition rate of 50 kHz were used for the laser scribing.

Electrical Results

A total of 24 full-area (156x156 mm^2) black Si solar cells were fabricated and compared with known data for KOH-textured cells. Due to reduced adhesion of screen-printed metal fingers at the edges of some of the black Si cells, the final cells were cut in 100x100 mm^2 squares in the edge isolation. The adhesion issues on RIE-textured Si will be investigated further in future studies.

Figure 6 shows the current density-voltage characteristic for 3 different black Si solar cells and the KOH-textured reference cell and quantum efficiency for one black Si cell compared to the reference cell.

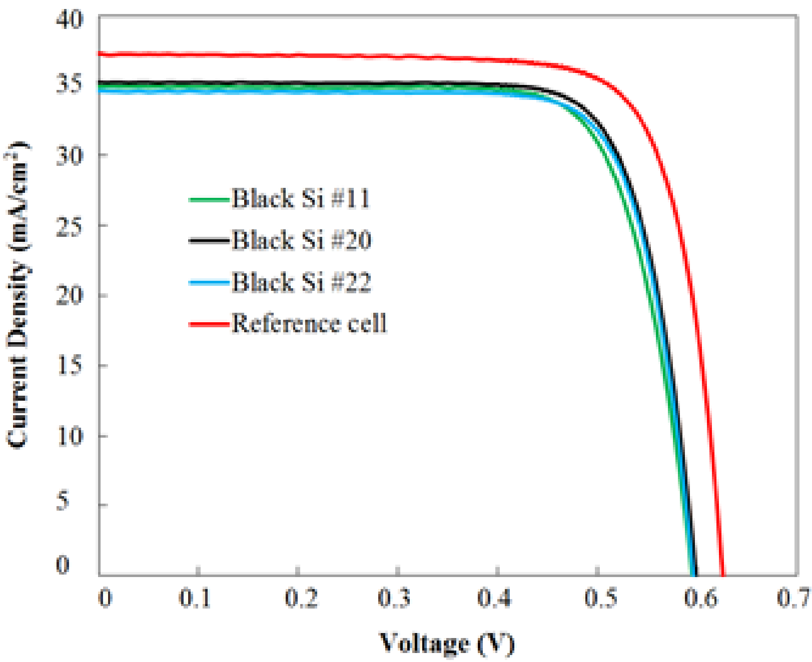

Figure 6: Current-density voltage (J-V) characteristic for 3 different black Si cells and a KOH-textured reference cell.

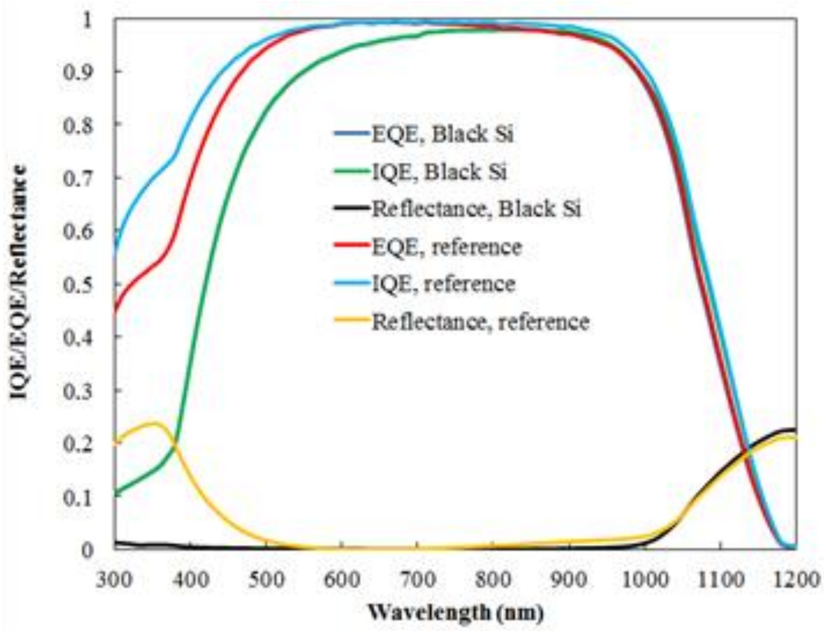

Figure 7: Internal (IQE) and External (EQE) Quantum Efficiency and reflectance as function of wavelength for the black Si cell (#11) and the KOH-textured reference cell.

Table 1: Short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), power conversion efficiency and series resistance (R_s) of 3 different black Si solar cells and a KOH-textured reference. The series resistance was extracted from EL and PL images.

Cell	**J_{sc} (mA/cm^2)**	**V_{oc} (V)**	**FF (%)**	**Eff. (%)**	**R_s (Ωcm^2)**
BS #11	34.93	595	75.67	15.73	1.07
BS #20	35.25	598	76.91	16.22	1.03
BS #22	34.62	596	77.32	15.95	1.04
Ref cell	37.31	625	77.09	17.99	0.88

Figure 6 and
Table 1 show that the black Si cells have power conversion efficiencies in the range of 15.7-16.3%. The 3 cells shown in Figure 6 and Table 1 represent the best, worst and mean of the 24 fabricated cells. The efficiency of the black Si cells is lower than that of the KOH-textured reference cell. Table 1 show that the lower efficiency is primarily due to lower J_{sc} and V_{oc}. Furthermore, the IQE measurement in Figure 7 shows that the lower efficiency of black Si cells is primarily due to increased carrier loss at wavelengths below 600 nm probably due to increased surface and emitter recombination. This was expected since previous studies show similar results and since no further attempt of optimization was made in terms of improved passivation or emitter quality.

<u>Black Ribbons</u>
In order to obtain an all-black appearance of cells and panels, black Si may be combined with black interconnecting ribbons. The cell results reported in this work did not involve these strings. Three different processes for blackening the ribbons were investigated. NiZnS and NiCuCo alloys, respectively, were deposited directly on Cu ribbons with soldering coating. Cu ribbons with a black oxidized surface were realized by a chemical oxidation process. Electroplating was conducted in a beaker with electrolytes containing sulfate salts and a nickel anode. Reflection measurements on the bare and coated surfaces were performed using a spectrophotometer (Shimadzu 2600).

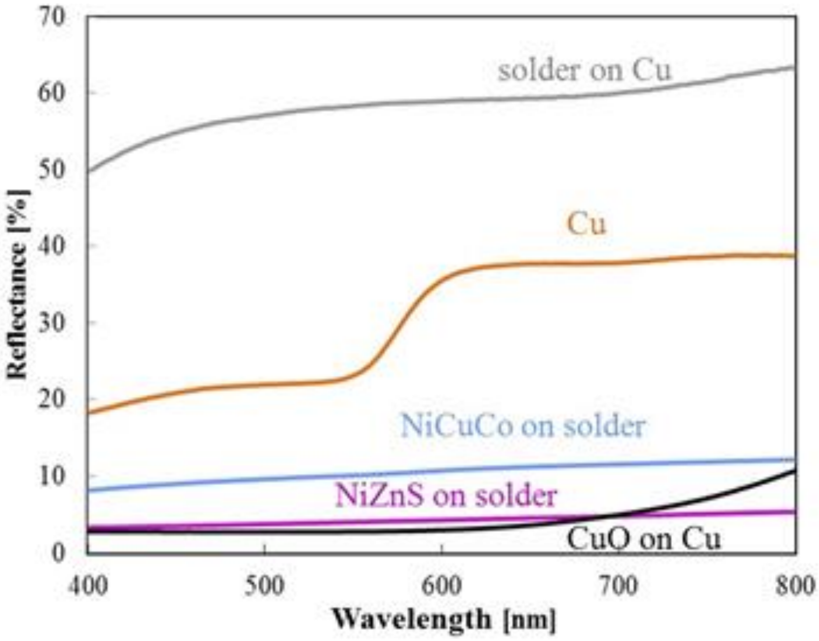

Figure 8: Measured reflectance as function of wavelength of interconnecting ribbons without (bare Cu, and Cu with solder) and with (NiCuCo, NiZnS, and CuO) black coatings.

Figure 8 shows the measured reflectance of the different ribbons. Reflectance of the strings with solder is high due to the bright metal surface, while the copper surface has a lower reflectance which increases for wavelengths above 600 nm. All of the blackened ribbons have significantly reduced reflectance. NiCuCo appears gray and has a higher reflectance compared with the other blackened ribbons, also, the reflectance of NiCuCo increases slightly towards longer wavelengths. The reflectance curve for NiZnS is quite flat and has a dark grey appearance. Oxidized Cu has the lowest reflectance, which increases slightly at longer wavelengths; indicating that the surface color has a red element due to Cu presence in the coating or due to the Cu substrate. In summary, Cu ribbons strings with CuO is the best match for black silicon with respect to the all-black appearance, because of the comparatively low reflectance.

<u>Complete Test Panel</u>
Finally, the black CuO-coated and etched busbar strings were used to connect screen-printed black Si solar cells into 4- and 9-cell test panels. Figure 9 shows a photograph of one of the produced panels.

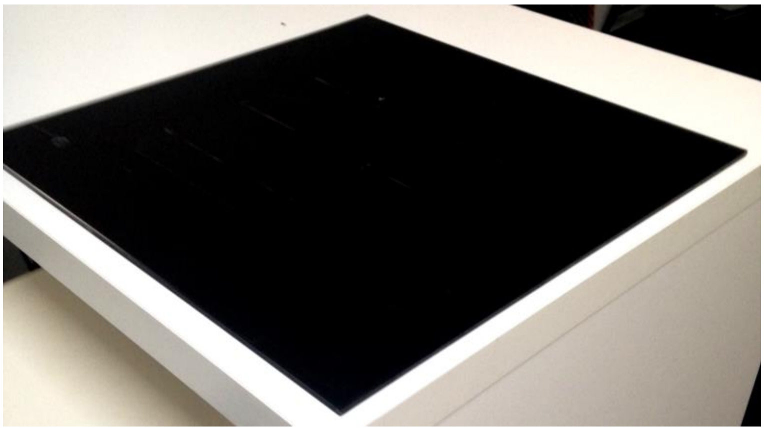

Figure 9: Photograph of a 4-cell panel based on screen-printed black Si solar cells and interconnected with black CuO-coated bus-bar strings.

In order to verify the electrical properties of the black bus-bar strings, current-voltage characteristics of two differently interconnected 9-cell test panels were performed. We used conductive glue for the CuO-coated bus-bar strings, since soldering was not possible for the given batch of strings. For comparison the more reflective etched bus-bar strings were interconnected by soldering to similar black Si cells from the same batch. The resulting IV-measurements are shown in Figure 10.

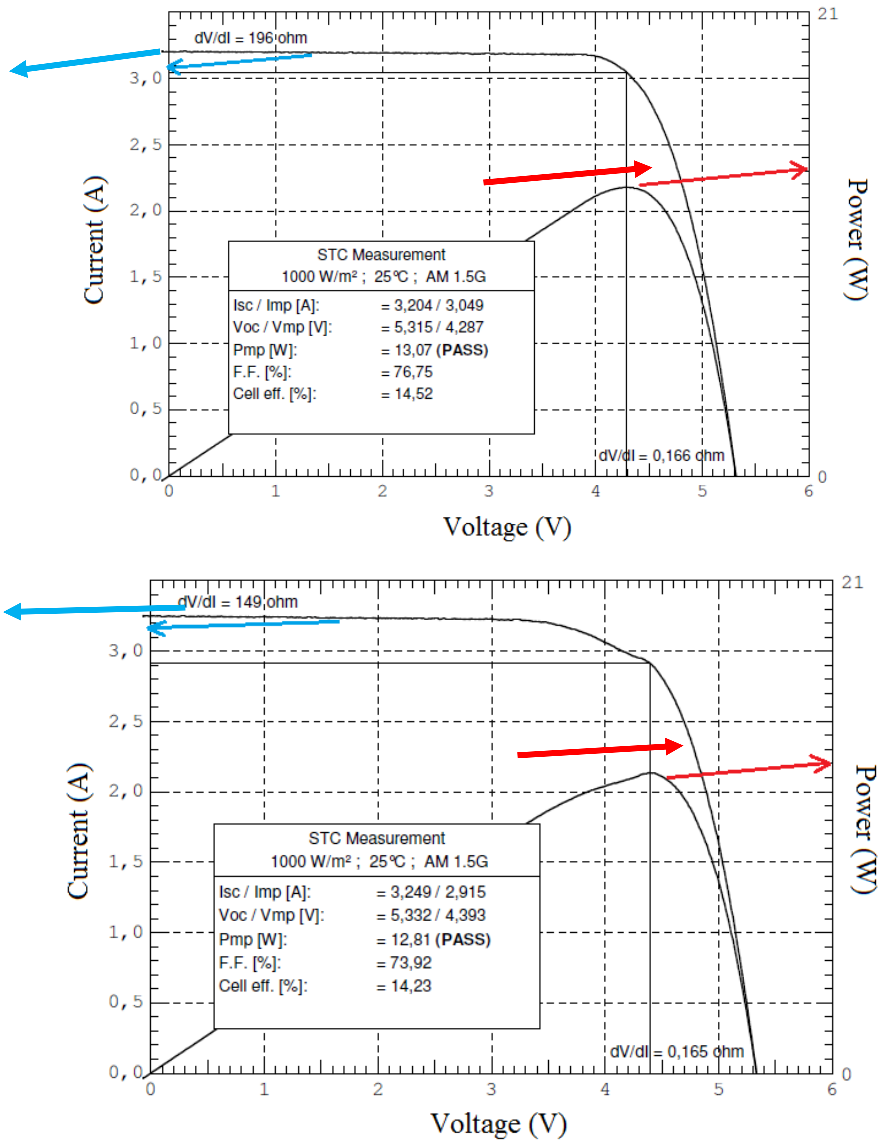

Figure 10: Current-voltage (I-V) and power measurement of two 9-cell test panels based on black Si solar cells interconnected with (top) soldered etched bus-bar strings and (bottom) glued CuO coated strings.

Figure 10 shows that both glued CuO- and soldered etched bus-bar strings gives acceptable fill factors of ~ 0.74 and ~ 0.77, respectively. Based on the calculated resistances on both sides of the maximum power point, the difference does not seem to be due to series resistance, but rather a slightly lower shunt resistance of the glued module and the non-ideal 'kink' on the I-V curve close to the maximum power point of the glued module. The detailed reason for these differences needs to be investigated further in the future. However, these data suggest that the soldered etched bus-bar strings yield higher fill factor, presumably due to the soldering rather than the effect of the coating itself. On the other hand, Figure 8 shows that the CuO-coated strings result in the lowest reflectance of the tested coatings. Thus the ideal solution would probably be CuO-coated bus-bar strings interconnected by soldering or an improved gluing process. This will be investigated further in future work.

Dissemination

The above results were disseminated at three different conferences: NSCC, Oslo, May 31-June 1, 2016, IEEE PVSC in Portland, US, June 5-10 2016 and EUPVSEC, Munich, Germany, June 20-24 2016.

Black silicon solar cells with black bus-bar strings, Davidsen, Rasmus Schmidt; Tang, Peter Torben; Mizushima, Io; Thorsteinsson, Sune; Poulsen, Peter Behrensdorff; Frausig, Jesper; Nordseth, Ørnulf; Hansen, Ole, part of: Proceedings of 43rd IEEE Photovoltaic Specialists Conference, 2016, IEEE, Presented at: 43rd IEEE Photovoltaic Specialists Conference, 2016, Portland, Oregon

Black Silicon Solar Cells with Black Ribbons, Davidsen, Rasmus Schmidt; Tang, Peter Torben; Mizushima, Io; Thorsteinsson, Sune; Poulsen, Peter Behrensdorff; Frausig, Jesper; Nordseth, Ørnulf; Hansen, Ole, part of: Proceedings of the EU PVSEC 2016, 2016

Black silicon with black bus-bar strings, Davidsen, Rasmus Schmidt; Tang, Peter Torben; Mizushima, Io; Thorsteinsson, Sune; Poulsen, Peter Behrensdorff; Frausig, Jesper; Nordseth, Ørnulf; Hansen, Ole, Norwegian Solar Cell Conference 2016, 2016, Oslo

1.6 Utilization of project results

The project results have been heavily exposed both in the 3 scientific publications/conferences shown above but also at commercial exhibitions. The images (Figure 11) below shows probing of all black PV BIPV modules at Building Green 2015. The interest was huge and it is definitely spot on what is demanded for.

Figure 11 – Exhibition of Black panels on Building Green 2015. Lower left shows the panel developed in this project.

A permanent installation is built at Gaia Solar's exhibition where the project prototypes is shown and updated as the project has progressed for get as much feedback as possible during the project.

It has proven a proof-of-business and it will be realized in the newly granted EUDP 64016-0030 addressing cost efficient production, reliability, scaling up and the commercialization starting October 1st 2016.

The project group has explored the possibility of patenting the combination of black strings and black silicon, and a novelty study showed a very narrow field that might be patentable, if very specific processes were used for obtaining the black strings. It was though concluded being almost impossible to enforce if granted and it was decided not to invest more in this track. There is though several better possibilities of IPR to be pursued in the next project.

The project results will primarily be used for a successful phase 2 project.

1.7 Project conclusion and perspective

The project has successfully solved the objectives and shown both proof-of-concept and proof-of-business of an all-black solar panel based on black silicon and black strings. Several electrochemical methods have been pursued to make the strings black and though not perfect the reflectance has been lowered significantly by more than a factor 10. Some approaches is better than others to achieve low reflectance. NiCuCo appears gray and has a higher reflectance compared with the other blackened ribbons, also, the reflectance of NiCuCo increases slightly towards longer wavelengths. The reflectance curve for NiZnS is quite flat (see figure 12) and has a dark grey appearance. Oxidized Cu has the lowest reflectance, which increases slightly at longer wavelengths; indicating that the surface color has a red element due to Cu presence in the coating or due to the Cu substrate. In summary, Cu ribbons strings with CuO is the best match for black silicon with respect to the all-black appearance, because of the comparatively low reflectance but reacts with the laminate and form gas bubbles. So some optimization is still to be done, but the time to upscaling is not far away.

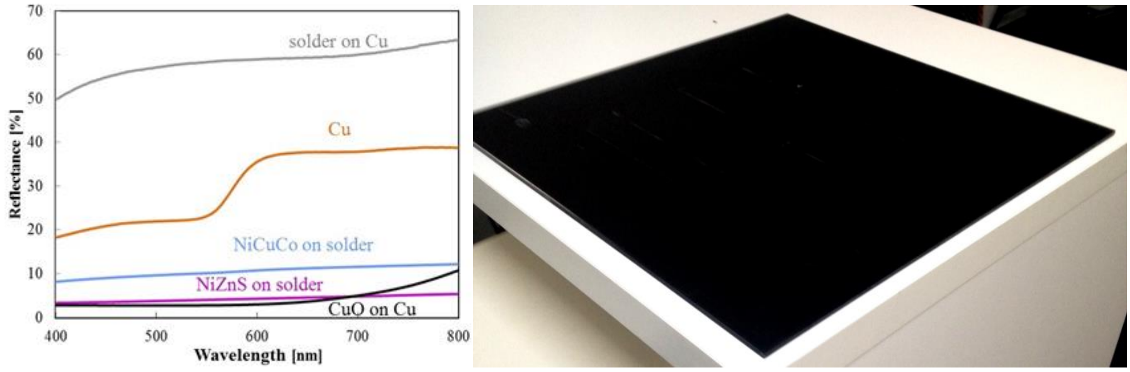

Figure 12 – Left, Measured reflectance as function of wavelength of interconnecting ribbons without (bare Cu, and Cu with solder) and with (NiCuCo, NiZnS, and CuO) black coatings. Right, Photo of all-black prototype of black silicon cells with treated interconnected ribbons.

Black silicon cells has been produced and implemented in prototype panels and the most successful one is shown in Figure 12 to the right. The dissemination processes has led to high both scientific and commercial interest. On the latter Meyer Burger (producers of process equipment for solar cell production lines) has contacted the project group with specific interest in having their process equipment tuned/developed to be able to produce black silicon and deliver process equipment being able to integrate such a process industrially. Furthermore, other panel producers are interested in being able to produce the black silicon panels.

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