FORTROLIGT NOTAT

Dato : 5/3 2014
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Distribution : Jens Windeleff, EUDP sekretariatet
Vedrørende : Oprensning af silicium til solcelleformål FASE2 Jnr 64012-0201 - slutrapport

1. BAGGRUND

EUDP har givet økonomisk støtte til FASE2 af projektet "Oprensning af silicium til solcelleformål" der i løbet af 14 måneder med projektstart 1. januar 2013 har arbejdet på at udvikle og validere en ny proces til oprensning af silicium fra Metallurgisk renhed til Solar Grade renhed.

Denne rapport beskriver projektets resultater herunder hvorledes indfrielse af de opstillede milepæle kan dokumenteres. Der bliver detaljeret redegjort for de udfordringer der er opstået i f. t. fremstilling af tilstrækkelige mængder af materiale til gennemførelse af den planlagte validering samt for de planer der er udarbejdet m.h.p. at sikre en hurtig realisering heraf i opstarten af projektets FASE3, som igangsættes pr. 1. marts 2014.

Indholdsfortegnelse

2. PROJEKT PLAN

Projektet har fulgt nedenstående projektplan, som i det følgende vil blive gennemgået og kommenteret.

Purification of silicon for solar cell applications PHASE2	Phase#2A:Verification									Phase#2B: Validation				
Start date: 01.01-2013	1	2	3	4	5	6	7	8	9	10	11	12	13	14
WP3 - Establishment of research lab	Phase#2A:Verification									Phase#2B: Validation				
WP 3.1 - Silane decomposition equipment modification														
WP 3.2 - Lab facility - installation and re-start operation														
Milestone 3: 100 g Si produced (verification of re-established research lab functionality)														
WP4 - Process development	Phase#2A:Verification									Phase#2B: Validation				
WP 4.1 - Process documentation														
Milestone 4A: All processes fully documented														
WP 4.2 - Knowledge transfer and supervision														
Milestone 4B: Most important know-how & know-why transferred to DK team														
WP 4.3 - Process development: Raw mtls preparation, Alloying, Synthesis & Decomposition														
Milestone 5: ½-1 kg of SoG Silicon produced (Product verification)														
WP 4.4 - Process optimisation: Raw mtls. Prepared., Alloying, Synthesis & Decomposed.														
Milestone 6: 50 kg of SoG Silicon produced (Optimised process w.r.t. yield & purity)														
WP5 - Validation of technology	Phase#2A:Verification									Phase#2B: Validation				
WP 5.1 - Lab scale verification of product usefulness														
Milestone 7: Silicon conformance to PVG-I spec verified. (Chemical analysis & SC@16%)														
WP 5.1 - Industrial scale verification of product usefulness														
Milestone 8: Industrial sized Solar Cell of min. 16% efficiency demonstrated														
WP6 - Business Case	Phase#2A:Verification									Phase#2B: Validation				
WP 6.1 - IP protection														
WP 6.2 - Cost modelling and verification of cost assumptions														
WP 6.3 - Development of Business Case														
Milestone 9: Business Case fully described - Final report														
WP 6.4 - Design input for industrial plant - a PHASE3 activity														
Milestone 10: Full scale facility fully designed														
WP7 - Project management	Phase#2A:Verification									Phase#2B: Validation				
WP 7.1 - Project management & reporting														
WP 7.2 - Follow-up on Critical Success Factors														
WP 7.4 - Budget controlling & Strategy modelling														

Figur 1, Projektplan med milepæle opdateret pr. 31/5 hvor anlæggets begrænsede produktionskapacitet først blev identificeret.

3. STATUS FOR DE ENKELTE ARBEJDSPAKKER

WP3 - ESTABLISHMENT OF RESEARCH LAB

WP 3.1 - SILANE DECOMPOSITION EQUIPMENT MODIFICATION

Objective	To implement a new method and new equipment for silane decomposition
Key Success Factors (KSF)	New silane destructor implemented and new desctruction principle demonstrated
Background	The first generation destructor based on a Free Space Reactor principle was observed to have limitations with respect to silicon particle size. This problem was realised during the commissioning test of the research lab in Kiev and it was decided, that we should not move the lab to Denmark before this issue was solved. Although it was made clear from EUDP, that funding from PHASE2 could not be released before the research-lab was transferred to Denmark, we took the full risk to fund this equipment upgrade ourselves while delaying the transfer of the facility to Denmark. The new destructor is based on the principles of Chemical Vapour Deposition (CVD) on an inductively heated silicon seed wafer and first had to be designed, constructed, implemented and tested.
Activities	The new destructor must be designed, constructed, implemented and tested.
Status: 27/2-2014	A new destructor principle has been design, constructed, implemented and tested. The originally implemented silane destructor where based on a principle where the silane molecules are destroyed when they are heated to above 700 °C in a hot steel tube (equivalent to the principles of a free-space reactor) - it's well known that this destruction principles will generate very small silicon fines that cannot easily be melted in the customer process. In the new destructor a pure substrate wafer are inductively heated in a "cold" quartz tube environment whereby the silane molecules are destroyed only when they see a hot silicon wafer, whereby the silicon are deposited in thin layers under controlled conditions (only on the wafer). This system works well and ensures that silicon can be produced under conditions where the chemical purity can be ensured - but unfortunately quite slowly. Although we knew that this destructor principle cannot be used on industrial scale, we still expected that it would be possible to produce some kg's of silicon with this set-up (enough for the validation activities). Unfortunately we later discovered that not even a few kg's can be produced, and we currently still limited to a maximum production of only 10-30 grams pr. day with this set-up.

WP 3.2 - LAB FACILITY - INSTALLATION AND RE-START OPERATION

Objective	To establish the research lab and demonstrate that it can operate and reproduce previously obtained results
KSF	Research lab is established and previously obtained results can be reproduced.
Background	After dismantling, transporting and reconnection it may be the case that some equipment has been contaminated or otherwise changed its properties. Also the new utilities (argon supply, power, ammonia etc.) may introduce new conditions. It's relevant to verify that everything once again works according to expectations.
Activities	Reconnect and ramp-up of equipment. Preparation of test-run to verify previously obtained quality and results.
Status: 27/2-2014	It's been quite a job to re-establish the research facility. Besides the specific pieces of equipment, also facility issues like DK regulations on electrical infrastructure, handling of cooling agents, water tightness of roof etc. had to be dealt with. Also a significant rearrangement of the gas-piping system was done, whereby a new purification step could be introduced and increased control of the individual gas-sections were provided e.g. by more argon flushing opportunities.

MILESTONE 3: 100 G SI PRODUCED (VERIFICATION OF RE-ESTABLISHED RESEARCH LAB FUNCTIONALITY)

Milestone completion	Several experiments have been completed during April and May where all steps in the process chain were performed fully in Denmark. This includes raw-materials preparation, synthesis of silane, gas purification and silane to silicon decomposition. In specific; experiment D1 on May 27 produced 25 grams of silicon fines and experiment D2 performed on May 29 generated 32 gram og silicon & fines.

WP4 - PROCESS DEVELOPMENT

WP 4.1 - PROCESS DOCUMENTATION

Objective	To ensure that all information required in order to operate the equipment are documented in English
KSF	All process steps can be operated by Danish team without presence of UA team
Background	The Danish team must learn how to operate the equipment safely and correct in order to achieve the same results as has been previously obtained in Kiev. Hereafter we can start to upgrade and modify the equipment according to ideas of the Danish team and availability of parts and pieces
Activities	First draft operation instruction is presented to DK team that through questions and questions and trials provide information required to rewrite the manual into a version that can be understood by DK team members
Status: 27/2-2014	All process elements has been documented and described in form of a SOP (Standard Operating procedure) as well as more detailed technical descriptions in text, calculation formulas and diagrams

MILESTONE 4A: ALL PROCESSES FULLY DOCUMENTED

Milestone completion	SOP's, drawings, process diagrams etc. has been prepared

WP 4.2 - KNOWLEDGE TRANSFER AND SUPERVISION

Objective	To ensure that all essential know-how and background knowledge are made available to DK team and documented in order to make the DK team capable of performing upgrades and modifications on their own.
KSF	All know-how and knowledge in general has been documented and understood by the DK team
Background	After many years of research into the NAIG process, a lot of knowledge and experience has been developed within the team. Some of this knowledge has been embedded in the equipment and process recipes whereas other elements are undocumented or documented in a way that is impossible for others to read, understand and work with.
Activities	The process details and general knowledge has to be documented and this information shall be transferred and shared among all team members.
Status: 27/2-2014	The Danish team has learned to operate all elements in the process sequence to a level where we also independently can adjust and improve operational, practical, technical and scientific elements of the process sequence. Whereas the old Professor S. Tarasevich does have long experience and in-depth chemical knowledge that we may also in the future benefit from, we do not expect that any other individuals in the original Ukraine team possess important and relevant knowledge that we do not already have or can get access to otherwise.

MILESTONE 4B: MOST IMPORTANT KNOW-HOW & KNOW-WHY TRANSFERRED TO DK TEAM

Milestone completion	The Danish team by now have developed an in-depth understanding of the process operation as well as the basic principles of the various chemical processes. The Danish team are convinced that we in several areas already have bypassed the original team both in areas of specific knowledge and by being able to team up with external knowledge resources among the world's most knowledgeable individuals in this area. In conclusion we are not any longer dependent on Ukraine research team, but might still benefit from continued collaboration and discussions with Dr. S. Tarasevich

WP 4.3 - Process development: Raw mtls preparation, Alloying, Synthesis & Decomposition

Objective	To demonstrate that the installed equipment can produce Solar Grade purified silicon.
KSF	Silicon purified to SG has been demonstrated when operating the equipment in Denmark.
Background	We already know that silicon fines can be produced with low B & P content. We need to demonstrate that the process also can generate Silicon in versions that comply with the definition in the Semi standard as PVG Silicon. Both purity and physical form is of importance
Activities	Process developments include upgrade of equipment, part wise PC controlled operation and automatic data collection for most important Process Indicators (temperature, pressure, flow rate, purity). Dedicated experimental investigation of process window with optimal yield and purity performance shall be investigated. Limitations of current technical solutions shall be identified and improved solutions implemented
Status: 27/2-2014	Significant effort has been put into the process development which has been closely integrated with activities to upgrade the equipment. With respect to raw materials a dedicated sub-project has been initiated where the crystal-chemical properties of the Mg_2Si alloy are investigated by IPU at DTU leading to further optimisation and process improvement (incl. improved understanding) at NAIG. Also significant effort has been made to obtain a stable and reliable decomposition process, which required various upgrades of sealing, gas-flow management, carbon susceptor encapsulation method as well as repair of inductor power generator

Milestone 5: ½-1 kg of SoG Silicon produced (Product verification)

Milestone completion	As is evident in the status description above, significant effort has been made to understand, optimise and upgrade the equipment, all leading to the process development expected. In specific many process changes and optimisation actions has taken place with respect to the synthesis, purification and decomposition as illustrated also by the change of gas-piping, introduction of extra borane filters, new types of flat-plate heat exchangers etc. As an outcome of these activities pure silicon has been made in smaller quantities with overall conformance to the Milestone requirements

WP 4.4 - Process optimisation: Raw mtls. PREPARED, Alloying, Synthesis & Decomposed

Objective	To demonstrate that the installed equipment can produce Solar Grade purified silicon.
KSF	Silicon purified to SG has been demonstrated when operating the equipment in Denmark
Background	We already know that silicon fines can be produced with low B & P content. We need to demonstrate that the process also can generate Silicon in versions that comply with the definition in the Semi standard as PVG Silicon. Both purity and physical form is of importance
Activities	Process optimisation basically resembles process development as described in the WP4.3 but with the increased ambition level, that Key Performance Indicators related to e.g. purity and yield must be improved

Status: 27/2-2014	Based on development activities performed in WP4.3, an additional optimisation effort has been made resulting in improved purity and yield. This is the case both with respect to raw materials preparation where the process now consistently generate a high quality product with a high yield of more than 90%, the synthesis operation can be completed within an 9 hours one-day cycle, the purification operation can be handled with much fewer stops required and the decomposition is now operated in a stable, reliable and consistent operation with increased yield

MILESTONE 6: 50 KG OF SOG SILICON PRODUCED (OPTIMISED PROCESS W.R.T. YIELD & PURITY)

Milestone completion	As described above the process has been successfully optimised with respect to alloying, raw materials quality and yield, synthesis operational process time, gas purity and deposition efficiency. Unfortunately, despite these optimisation results we're not able by-pass the fundamental bottleneck represented by the optimised Chemical Vapour Deposition process of silane by use of our non-contact and non-contamination inductor principles. The limitations in absolute production capacity of the facility was discussed already during a steering committee meeting on May 31 2013, when it was still unclear exactly how low the capacity of the facility would end up. Around august 2013 it became clear, that we would never be able to produce neither 10 nor 50 kg of silicon in the present setup. As a consequence we decided to organise the application (with deadline one month later) for PHASE3 of this project around the theme "up-scaling" as we realised that only in case the equipment design was fundamentally changed and new solutions implemented, it would be possible to fully comply with the PHASE2 Milestone #6 by producing 50 kg of SOG silicon

WP5 - VALIDATION OF TECHNOLOGY

WP 5.1 - LAB SCALE VERIFICATION OF PRODUCT USEFULNESS

Objective	To verify that the material produced actually is PVG-I quality and can be used for solar cell manufacturing
Responsible	Jan Vedde
KSF	Purity of Si-PVG-I verified and solar cells of minimum 16% efficiency has been manufactured
Resources	External partners and labs
Background	After the first few months of operation and process optimisation it's expected that at least 1 kg of solar grade material will be produced. This usefulness of this material for the intended purpose has to be verified in the Work Package
Activities	The material produced will be send to external partners for crystallisation test and samples will be taken for chemical analysis. If considered reasonable and realistic also small lab scale solar cells will be made - if equipment that can handle the small size silicon wafers can be identified.
Status: 27/2-2014	We already very early in the project supplied small quantities of silicon fines to the German Institute für Krystalzüchtung (IKZ) where they managed to grow a very small silicon crystal from our material. This was the first indication that the product can be used for crystallisation, despite the fact that fines normally cannot be handled by crystallisation operators

MILESTONE 7: SILICON CONFORMANCE TO PVG-I SPEC VERIFIED. (CHEMICAL ANALYSIS & SC@16%)

Milestone completion	With respect to conformance to PVG-I spec, we have quite good results as can be seen in the table in chapter 5. Based on the latest chemical results obtained from Silicor Materials lab in Berlin, the product purity conform to not only the "lowest" class I type of material but actually qualify as a class III type of material when assessing the important factors of Boron and metals. Phosphorous obviously still is much too high in concentration, but we've identified a solution for this problem which are known to work when used in competitor facilities, so we're confident that this issues also will be solved at our facility within the coming few months. With respect to solar cell manufacturing, we unfortunately are not able to deal with this task as the overall quantities of material produced are too small to be converted into ingots, wafers and cells as otherwise planned

WP 5.1 - Industrial scale verification of product usefulness

Objective	To verify that the material produced in large quantities conform to the requirements of Si-PVG-I quality and can be used for manufacturing of industrial ingots, wafers and solar cells
Responsible	Jan Vedde
KSF	Full industrial scale ingots of multi and/or monocrystalline quality has been manufactured and converted into crystals, wafers and solar cells according to standard expectations within the solar industry
Background	After optimisation of the process according to knowledge about how to obtain the optimal purity, yield, consumables efficiency and productivity, the equipment must be run under those conditions for some time in order to generate knowledge on eventual challenges related to operation of the equipment and process under continuous conditions
Activities	The NAIG process has to run over quite some time to generate knowledge about full-scale productivity issues and in order to generate enough material to be able to complete the following validation test
Status: 27/2-2014	This work package was formulated in august 2011, when the research lab was still under construction in Kiev. At this stage in the project, it was a clear ambition and design criteria, that the facility should be able to produce quantities sufficient for industrial validation. As described above, the overall project has progressed quite positively, with the clear exemption that production capacity targets cannot be met in the existing facility due to a bottleneck in the CVD equipment. This challenge has been addressed as the central focus area in the FASE3 of the project, but can unfortunately not be dealt with in the actual project (FASE2)

Milestone 8: Industrial sized Solar Cell of min. 16% efficiency demonstrated

Milestone completion	As described under Status above, it's not possible to produce the required quantities of material necessary for an industrial validation which therefore cannot be completed until PHASE3 of this project

WP6 - Business Case

WP 6.1 - IP protection

Objective	Ensure that IP are carefully protected
Responsible	PK & JV
KSF	Important process and equipment knowledge are developed and protected through patents or otherwise.

Resources	S. Tarasevich, Inspicos
Background	First international patent has been filed but additional patents may be required to protect the IP
Activities	Protect our IP by operating in stealth mode and file patents
Status: 27/2-2014	A patent that describes both purification and yield enhancement principles of relevance for achieving good results when using the NAIG purification route has been filed and accepted. All IP rights originally residing in Ukraine has now been legally transferred to the Danish company North Atlantic Innovation Group.

WP 6.2 - Cost modelling and verification of cost assumptions

Objective	To develop a cost model that can be used to assess the cost potential
Responsible	Jan Vedde
KSF	A cost model has been developed and verified
Resources	External consultants
Background	An important KSF is the cost of manufacturing. We must demonstrate that we have a good understanding of the most important cost elements in our processing method
Activities	Develop and verify a cost model
Status: 27/2-2014	A detailed cost model has been developed, that address not only the cash cost (materials, energy, and labour) but also CAPEX involved the operation.

WP 6.3 - Development of Business Case

Objective	To collect updated information on the price-structure, technical and commercial market status for PVG-I silicon feedstock among manufactures and end-users.
Responsible	Jan Vedde
KSF	An understanding of key technical factors as well as cost structure for traditional and alternative manufacturing methods for PVG-I silicon has been established
Background	Jan Vedde already has a good knowledge and understanding on these issues but this is a very dynamic market with many new technologies for silicon purification under development worldwide. Also the existing market leaders with high production capacities are aggressively gaining market shares and improving their cost-structure by expanding operations
Activities	Follow-up in technical literature, conferences and commercial announcements. Discussions with key-stakeholders in the market and potential customers/end-users
Status: 27/2-2014	Since year 2000 Jan Vedde has followed the silicon market for solar closely both with respect to commercial and technical issues. A separate report that describes the current market situation and business case opportunities of NAIG has been prepared

Milestone 9: Business Case fully described - Final report

Milestone completion	A report that describes the current market situation and business case opportunities of NAIG has been prepared

WP 6.4 - Design input for industrial plant - a PHASE3 activity

Objective	To provide all design input for a full scale industrial production line
KSF	All required design input for an industrial line has been prepared

Background	Based on design experience from the current demonstration facility and additional learning's obtained when operating the demonstration line in Denmark and also additional ideas and concepts developed during the project, all conditions have been prepared for designing a fully integrated and optimised production line for purification of silicon
Activities	The concept for an integrated production line must be developed and the detailed process conditions and equipment designs must be engineered, drawings must be made and controlled/inspected/verified according to all relevant safety/security and other standards
Status: 27/2-2014	This important task was never meant to be included in PHASE2 of the project execution but will be one of the core focus area in the next phase of the project

MILESTONE 10: FULL SCALE FACILITY FULLY DESIGNED

Milestone completion	This activity incl. milestone has been moved to the PHASE3 of the project

WP7 - PROJECT MANAGEMENT

WP 7.1 - PROJECT MANAGEMENT & REPORTING

Objective	To ensure an efficient and smooth execution of the project
KSF	All project WP and milestones are executed according to time-schedule, budget and target objectives
Background	A detailed project plan with time-schedule and budget has been prepared. However once the project gets started we'll likely meet challenges and surprises where innovative and creative solutions are required. Project management must address the new situations.
Activities	Close follow-up on all project activities to ensure project is on-track with respect to activities, timing, budget, resources, project goals etc.
Status: 27/2-2014	Progress according to plan.

WP 7.2 - FOLLOW-UP ON CRITICAL SUCCESS FACTORS

Objective	To ensure that the project is continuously on track towards successful completion.
KSF	A detailed set of KSF has been identified and are tracked in a systematic and well defined way
Background	In order to be successful the project must progress along several different paths, not only the chemical purity of the silicon is important but also the ability to use the feedstock in a traditional casting furnace and mono crystal pulling process is important. In addition it must be verified that the overall Cost-of-Ownership of the process is competitive, which requires a detailed analysis of both the direct, indirect and capital cost structure. In addition environmental, safety and health issues must be clarified
Activities	All the issues mentioned above must be carefully analysed and an assessment must be made, to ensure that no clear stop-criteria for the project are overlooked.
Status: 27/2-2014	Progress according to plan.

WP 7.4 - BUDGET CONTROLLING & STRATEGY MODELLING

Objective	To ensure that the project is executed according to budget
Responsible	Peter Kolos
KSF	Project execution according to budget
Background	A rough budget has been prepared, however a lot of unknowns still exists with respect to the actually realised costs of equipment, facility etc.
Activities	Detailed budget controlling
Status: 27/2-2014	Progress according to plan

4. SOLAR GRADE KVALITET

For at kunne vurdere om det fremstillede materiale lever op til betegnelsen Solar Grade Silicon, har vi valgt at sammenligne vores resultater med de krav der opstilles i SEMI standarden PV-017-0611 for Solar Grade Silicon. I tabellen nedenfor har med gul markeringsfarve indsat gennemsnitsværdien af to målinger foretaget 19. december 2013 af Silicor hhv. 17. januar 2014 af Elkem Solar på silicium fra vores to sidste eksperimenter ”R7” og ”R8”.

Som det fremgår af tabellen, er vi i stand til at opnå en renhed der opfylder betingelserne for Solar Grade klasse III for både acceptorer, overgangsmetaller samt alkali og sjældne jordarter mens vi for kulstof kun opfylder betingelserne for klasse IV materiale.

Det eneste udestående problem er, som ovenfor nævnt, fosfor, hvor den målte koncentration for disse to prøver desværre ligger på hhv. 42.000 og 48.000 ppba desværre ikke opfylder kriterierne for solar grade. Som nævnt i rapporten har vi dog identificeret en løsning som adresserer dette problem som vi derfor forventer er løst indenfor få måneder.

Category:		**EG-Si**	**SG-Si I**	**SG-Si II**	**SG-Si III**	**SG-Si IV**
Acceptor concentrations (B, Al)	ppba	≤0.06	≤1	≤20	≤300 [147]	≤1000
Donor Concentrations (P, As, Sb)	ppba	≤0.3	≤1	≤20	≤50	≤720
Carbon	ppma	≤0.170	≤0.3	≤2	≤5	≤100 [43]
Oxygen	ppba	Not specified				
Transition Metal (Ti, Cr, Fe, Ni, Cu, Zn, Mo)	ppba	≤5.0	≤10	≤50	≤100 [64]	≤200
Alkali and Earth Alkali Metals (Na, K, Ca)	ppba	≤5.0	≤10	≤50	≤100 [92]	≤4000
Total Hydrogen & Chlorine concentration		low enough so that particles do not explode on heating				
Shape & size		Rods: length x diameter Bricks: length x width x height Chunks: ≤250 mm, Chips: < 50 mm Granules: 0.1-10 mm Powder: ≤ 500 µm			 **Figure 1 Silicon granules deposited on a silicon wafer.**	
Surface, surface appearance, oxide layer thickness		Grey clean dry surfaces, foreign material not allowed, low amount of brownish amorphous Si. For powders: ≤ 300 pm or ≤ 10 ppma physi- or chemisorbed partial surface monolayer layer				
Examples of suppliers		Hemlock, Wacker REC	Hemlock, Wacker, REC	REC, MEMC FBR	Elkem	Silicor Materials

Tabel 1 Produktspecifikationer for solar grade silicium iht. Semi PV-017-0611 samt vores sidste resultater [i gult]