

TECHNICAL EXPERIENCE DURING THERMAL AND CHEMICAL RECYCLING OF A 23 YEAR OLD PV GENERATOR FORMERLY INSTALLED ON PELLWORM ISLAND

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ABSTRACT: The disassembly of the 23 year old PV generator formerly installed on Pellworm Island offers the seldom opportunity to recycle a large amount of PV modules of the same design. The technical experience obtained during this recycling process is presented. The high quantity of nearly identical modules allows to investigate, to record and to evaluate the different types of damage of the modules and the recycling process systematically. The influence of module design and module damage on the results of the whole process as well as of several process steps like thermal and chemical treatment is described.

Keywords: Recycling, PV Module, Silicon

1 INTRODUCTION

The first German PV power plant, a 300 kW PV Generator (Figure 1) installed on Pellworm Island in 1983, was dismantled in summer 2005 because the solar field was modernized by EON-Hanse AG. 15,795 of the 17,568 modules of the Pellworm generator (Table 1) were transported to the recycling plant of Deutsche Solar AG and stored in containers prior to subsequent thermal processing.



Figure 1: PV generator on the German island Pellworm

via ultrasonic welding. Thereby two different kinds of ultrasonic welding were applied (see Figure 3).

Table 1: Technical data of the old Pellworm PV Generator with AEG PQ20 modules [1, 2]

| | |
|--|---|
| Year of construction | 1983 |
| Installed power in kWp | 300 |
| Module power in Wp | 17.1 ± 10% |
| Total number of modules | 17,568 |
| Number of recycled modules | 15,795 |
| Mass of a module in kg | 3.8 |
| Module dimensions in mm | 460x560 |
| Dimensions of Stainless steel frames in mm | 460x560x12 |
| Number of cells per module | 20 |
| Type of silicon cells | multicrystalline |
| Cell dimensions in mm | 100x100x0.4 |
| Connection | Cable at edge of module, noble steel frame, plug and socket interconnection, thyristor inverter |
| Year of shutdown | 1989 |
| Recycling and system rebuilt | 2005/6 |

2 DESIGN AND STATE OF PRESERVATION OF PELLWORM MODULES

The double glass modules are bordered with stainless steel frames. Their main dimensions are 560 x 460 x 12 millimeters. The modules were connected among each other via plug connectors as shown in Figure 2. Every module contains twenty multicrystalline silicon cells of 100 x 100 mm width and length and a thickness of about 0.4 mm. The cells are embedded in PVB. Most of the modules contain cells of the same type with a typical backside metallization of aluminium. Only few of the modules contained a different kind of polycrystalline cells in the same dimensions. These cells differed in backside metallization (silver) and grid. The cells of the Pellworm modules were connected with aluminium tabs

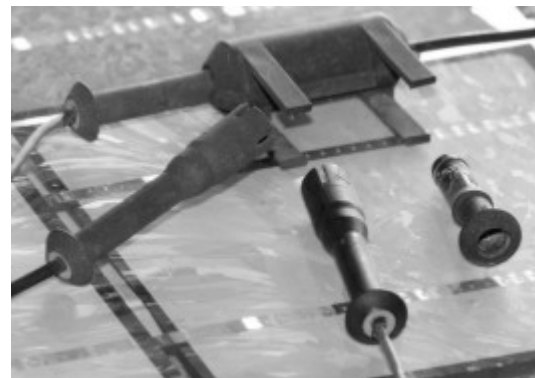


Figure 2: Plug-connection of AEG PQ20 modules

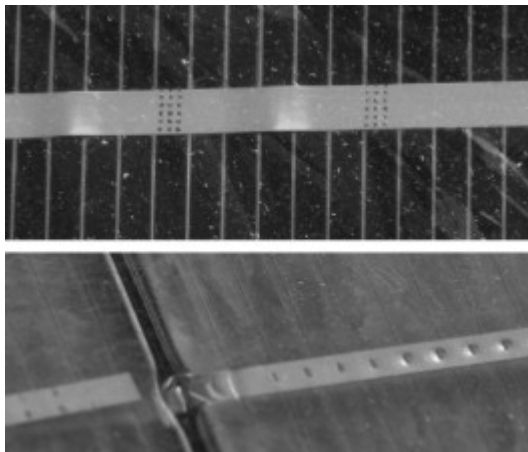


Figure 3: Different types of welding heads

Also two versions of cell arrangement or circuitry were found. About fifty percent of the recycled modules had defects of electrical insulation. Often the insulation of the connecting cables was degraded. This was one of the reasons for the early decommissioning of the PV-installation. In some cases the modules surface was particularly covered with moss and lichen (both Figure 4).

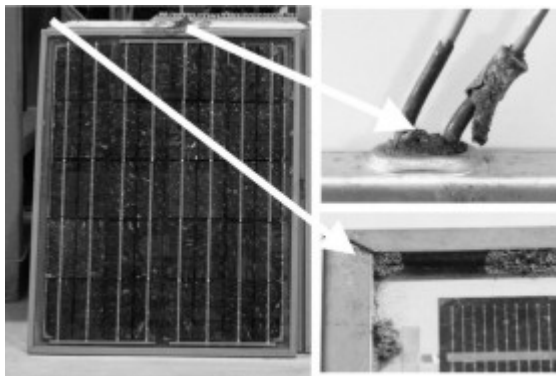


Figure 4: Pellworm-module with lichen on the border of the frame and defect electrical insulation

For a further evaluation of the state of preservation nearly 20% of the treated modules were inspected during the preparation for thermal treatment. The defects were classified in the following types:

- glass breakage
- the content of damaged cells
- laminate defects and
- defect electrical insulation

The frequency of these defects was recorded. The results of this screening are shown in Figure 5. About fifty percent of the recycled modules had visible defects.

Most of these defects did not affect the results of the recycling process observably. The amount of recovered cells of glass breakage modules was only 4 % lower compared with the amount of recovered cells from undamaged modules.

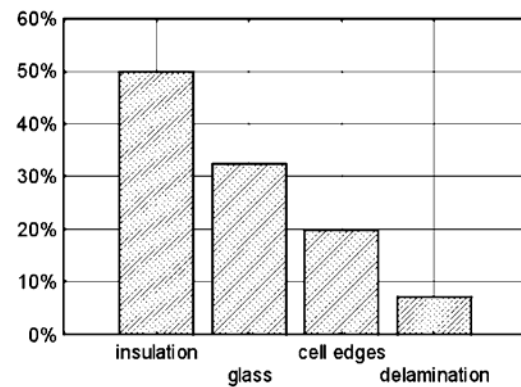


Figure 5: Reasons for modules damage

The main failures of slightly damaged cells were broken edges in the original laminates (see Figure 6). But also scratched and broken cells embedded in the module compound were found. Cells with damages could not be processed after the recycling. Thereby the final recovery rate decreases.

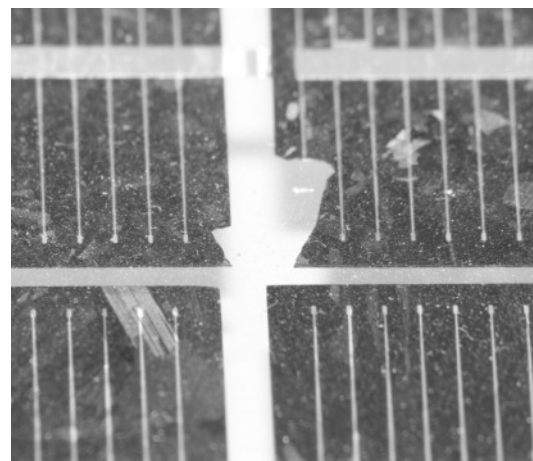


Figure 6: Cells with edge damage inside a module

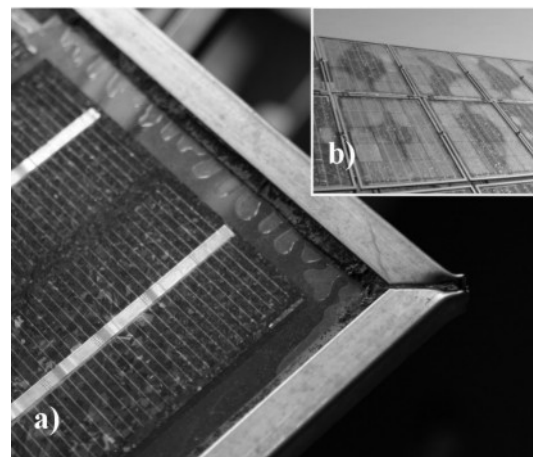


Figure 7: a) Delamination on the border area of a module b) discoloration of nearly complete modules

The whole decrease of the yield of intact cells caused by this reason was estimated of about 1.7 %.

Delamination and discoloration (laminate yellowing, and discoloration of antireflective coating) had no effect

on the results of thermal recycling and the amount of re-extracted cells. The laminate of discolored modules got a dark brown coloration. Delaminations were found most notably at the edges of the embedded cells (see Figure 7).

To examine the power loss due to aging three modules without glass breakage or defect electrical insulation were tested by a sun simulator in standard test conditions. An average reduction of 12 % could be asserted for the three samples.

3 RECYCLING PROCESS

Figure 8 surveys the recycling process of Deutsche Solar AG schematically. The process consists of two main steps. First the laminate is burned off to facilitate the manual separation. In case of crystalline silicon cells, the metallization, antireflective coating and p/n-junction were removed subsequently by etching. Solar cell recycling can be done by etching on a technical scale, the surface finish can frequently be adjusted to the customer's demands.

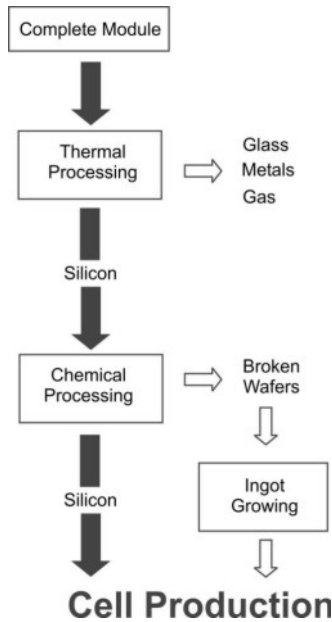


Figure 8: Principle of the Recycling Process of Deutsche Solar AG

4 THERMAL PROCESSING

Because there was no experience of recycling that type of modules, the thermal treatment recipe had to be optimized in several test series.

Process control of thermal treatment depends heavily on module design. The type of laminate and the module dimensions influence the course of the process.

The heat flux in the afterburner depends on exhaust gas emission during thermal process. Hence it is a gradient of reaction progress.

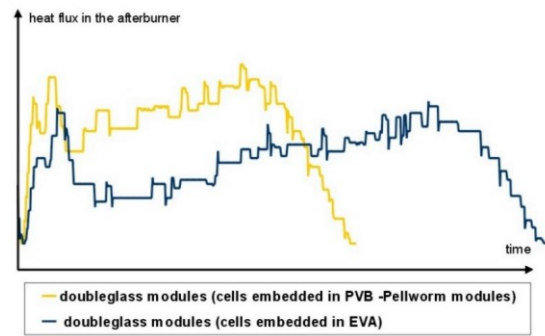


Figure 9: Heat flux in the afterburner during thermal process of Pellworm modules compared with that of double glass modules of other fabrication

The two curves in Figure 9 demonstrate the differences of the course of the process by treating Pellworm modules and double glass modules of another fabrication in comparison. The Pellworm modules contain PVB laminate the other module type has an EVA lamination inside. Though the dimensions of both module types differ notably, the amount of laminate, glass, and stainless steel during both thermal processes were nearly equal.

As it is visible in the diagram (Figure 9) the gas emissions during both furnace cycles differ considerably.

During a first thermal step the laminate of the Pellworm modules was burned off, the cells were set free and the modules could be separated in their recyclable constituents:

- intact cells,
- cell breakage,
- stainless steel frames and
- glass panes.

The small dimensions of the Pellworm modules and the relative great thickness of the embedded cells of about 0.4 mm effected in a yield of 84,9 % of intact cells.



Figure 10: Material separation after thermal process

The strong fastened interconnectors made of aluminium demanded a special handling and great carefulness in separation.

Because the interconnector tabs could not be detached easily from the cell surfaces, the cells had to be cut free before collecting them from the glass panes.



Figure 11: The Pellworm cells were cut free before collecting

After this a second thermal treatment was necessary to remove the ultrasonic welded aluminium interconnectors from the cells. In some cases the large and deep welding points at the cells surface resulted in holes, which became visible after the etching process.

5 CHEMICAL PROCESSING

The chemical treatment involved the separation of the metallization, the dissolving of the antireflective coating and the etching of the silicon wafers to remove the n-doped emitter. In several selective etching steps all these layers were removed subsequently with several mineral acids and acid mixtures. The etching recipes have to be adapted to the different cell technologies used for the Pellworm generator. Consequently there was no universal recipe which could be applied generally. Accordingly the process steps have to be modified. For instance a part of the Pellworm cells had a silver metallization which had to be removed by an acidic etching process only. The bigger part of the cells was coated with aluminium which required an alkali treatment in the first step. The process regimes had to be developed in such a way that the high electronic quality of the wafer was conserved. Before starting the next etching step, the completeness of the respective step when gradually taking off the layer is extraordinarily important for the pretreatment. Only in this way, a consistent etching attack on the next layer can be realized over the complete wafer surface in the further course of the process, which avoids underetching or the forming of etch pits.

In a first step the recycled wafers were characterized by a non-contacting resistivity measurement and a determination of the thickness. The average resistivity of the material was within a range of 1.8 to 2.9 Ωcm and the thickness of the wafers ranged from 400 to 450 μm .

One of the biggest problems laid in the history of the Pellworm cells, because the aluminium strings were hand-made ultrasonic bonded.

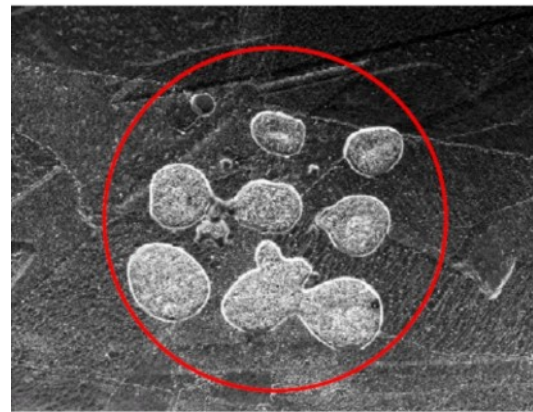


Figure 12: SEM/EDX investigations of the ultrasonic bonded wafer surface. The white points in the circuit were analyzed by the EDX method.

This generated deep holes in the wafer filled out with aluminium (Figure 12). To remove the metal a long etching time was needed in the NaOH solution. The principal task at this point was to optimize the etching temperature, time and alkali concentration in such a way that the silicon is only taken off as much as necessary.

Figure 13 shows the result of one etching experiment. The hole on the left side of the image was cleared of aluminium, whereas the hole on the right side is filled out with metal.

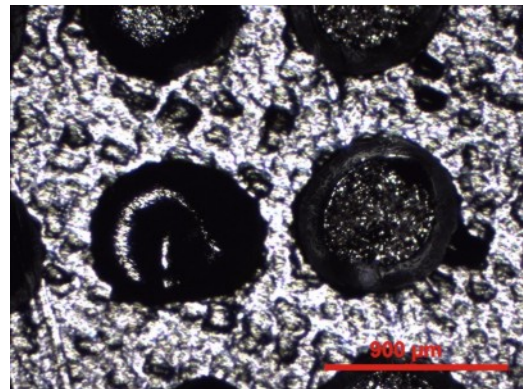


Figure 13: Results of etching experiments

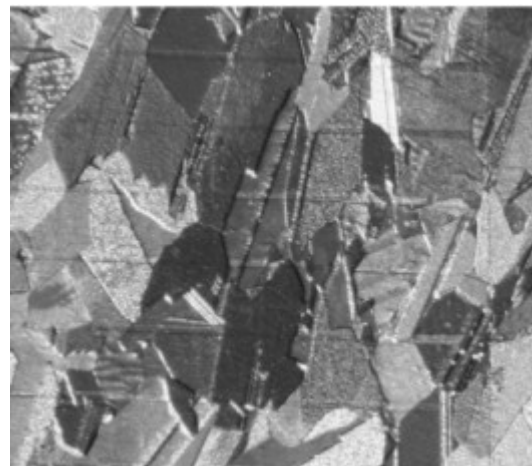


Figure 14: Visible unevenness of the wafer surface

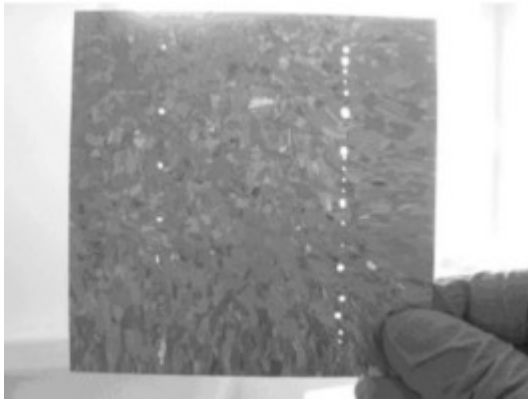


Figure 15: Holes visible after the etching process caused by large and deep welding points

Figure 14 shows visible unevenness on the surface of an etched wafer. These were already visible on the cell surface before etching. Measurements displayed, differences of level between 20 and 30 microns.

A too aggressive etching attack would generate etch pits and amplify differences in the surface morphology as a result of the anisotropic etching behavior of alkaline solutions. In the extreme case it could even form through-going holes (fig. 15). Obviously, in some cases the wafers were only a few microns thick at these bonding holes.

The further characterization of the recovered wafers coming from the optimized process was done by electrochemical CV measurements of the charge carrier concentration at the front side and life time mappings after an adequate additional cleaning procedure (Figure 16). The CV measurements depending on the depth showed that the emitter was removed completely and the results of lifetime mapping attested a good quality of the recycled wafer material.

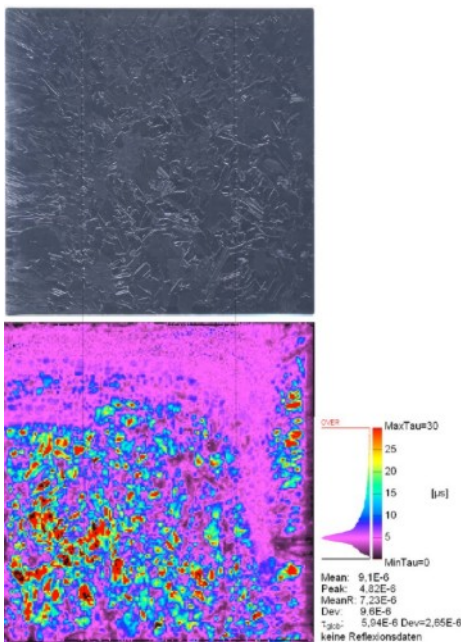


Figure 16: Scan of a wafer and the corresponding lifetime mapping by μ W-PCD. The average lifetime amounts 10 μ s.

6 ENERGY BALANCE

To get a first insight on sustainability of the recycling of the project an energy balance of the first lifetime of the Pellworm modules, their second lifetime (recycling included) and a common module was done. In Table 2 the assumptions for this calculation are shown. The Pellworm-modules were produced in the early eighties. No detailed data concerning their production is known. But the data published by Hagedorn [4] is representative for the technology. The data of the recycling, cell processing and module assembly is collected during the project. The performance of the recycled modules per m^2 is considerably higher than it was in the first lifetime, but lower than that of a module produced nowadays with new wafers. The calculation shows, that the modules had an Energy-Pay-Back time (EPBT) of seven years in their first lifetime (Figure 17) After 2 years the new modules will have generated the amount of energy that was necessary for their production.

Table 2: Assumptions for the energy balance

| | 1 st life-cycle | 2 nd life-cycle | common module |
|----------------------------------|----------------------------|----------------------------|-------------------|
| Irridation | 1000 kWh/kWp/yr | | |
| Performance ratio | 0,75 | | |
| Performance (Wp/m ²) | 80 | 134 | 142 |
| Data source | [5] [6] | own | [7] |
| Module | 20 cells à 100 mm | 72 cells à 100 mm | 72 cells à 125 mm |

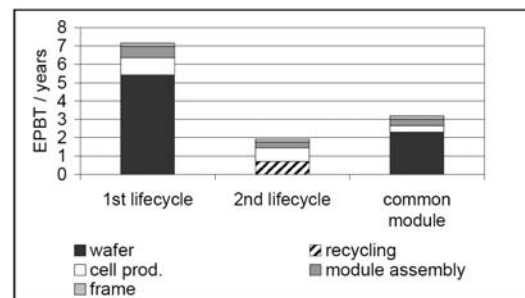


Figure 17: Energy Pay Back Time of the Pellworm-modules in the first and second lifetime and a common module.

7 SUMMARY AND RESULTS

The results of recycling the old Pellworm power plant are given in Table 3. The total amount of recycled modules from the Pellworm Generator was 15,795 modules containing 315,900 cells. That is equal to 252,720 Wp and an efficiency of 8%. The new generator completely made of recycling cells will have a performance of 237,589 Wp and an efficiency of 13%. That means that 94 % of the original performance of the old Pellworm Power Plant will be received.

Besides 3,263 t of stainless steel frames were sold and 487 kg cell breakage from module recycling and 149 kg from cell processing were collected for further processing in the growing of silicon ingots.

Table 3: Results of the recycling of the Pellworm Generator

| | Input | Output | yield | Yield cum. |
|---------------|---------|----------------|--------|------------|
| No of modules | 15,795 | 241,514 wafers | 76.4 % | 76.4 % |
| No of cells | 315,900 | 177,454 | 74.5 % | 56.1 % |
| Power in Wp | 270,095 | 237,788 | 88.0 % | |
| Efficiency | 8 - 9 % | 12 - 14 % | | |

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