RECENT IMPROVEMENTS IN INDUSTRIAL PV MODULE RECYCLING

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ABSTRACT : The considerable growth of the PV market that started 30 years ago, will lead to a fast growing number end of life modules. If good solutions for recycling are developed, a huge accumulation of this end of life and rejected PV modules can be avoided. The aim of this work was to develop and to evaluate different recycling processes. Finally two methods have given acceptable results namely the pyrolysis in a conveyer belt furnace and the pyrolysis in a fluidised bed reactor. Especially for the fluidised bed reactor process, the development has reached an industrial level with the set-up of a big pilot reactor. The cost effectiveness of the process is demonstrated by the high mechanical yield of the process and the high quality of the reclaimed wafers, as proven by a high cell efficiency after reprocessing. The ecological impact of recycling is very high and the energy pay back time decreases drastically due to the avoided high energy consumption of the reclaimed silicon wafer.
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1. INTRODUCTION

Related to the PV module shipments 20 to 25 years ago, the accumulation of end of life PV modules will increase very fast. The producers of solar energy, a clean energy source, cannot afford a landfill destination for their end of life PV modules. Due to the relative high value and energy content of the silicon wafers, a dismantling operation for used and rejected PV module can be cost effective and is environmentally justified by a very positive life cycle analysis. Industrial recycling processes are optimised followed by a silicon wafer reclaiming and an optimised silicon solar cell and module process. The high quality of the reclaimed silicon wafers is proven by the solar cell efficiency results after reprocessing using an adapted solar cell process.

2. OPTIMISATION OF RECYCLING PROCESSES

Different potential recycling processes were proposed in the beginning of the project. Some of them seemed not to be promising and further research was stopped in an early stage.

Pyrolysis with microwave heating failed due to the non-uniform temperature distribution resulting in a considerable cell breakage.

Also dissolving the modules in a chemical reactor with tri-ethylene glycol at temperature between 220° C to 290° C resulted in negative results. The EVA swells up and does not release from the module. Tests with other solvents came to the same conclusion [1].

Immersion in hot nitric acid had already shown its potential [2]. New tests based on earlier experience showed that, though the process works, it is unlikely to become a viable industrial process due to huge amounts of nitric acid needed. Disposal of this chemical waste in a responsible manner and the treatment of the toxic NO_2 gases would undoubtedly increase the cell recovery complexity and the energy involved as well as the financial cost significantly.

The thermal approach seems to be favourable to a chemical one [3]. Therefore, pyrolysis in a conveyer belt furnace looks promising as an industrial recycling process.

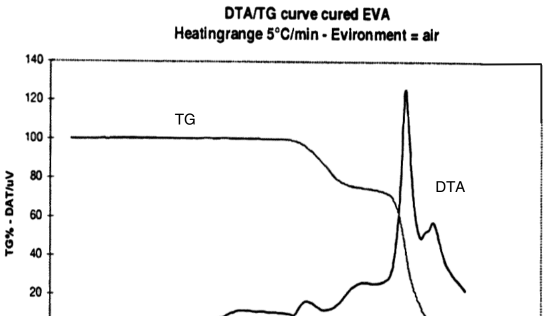


Figure 1a DTA/TG-curves from EVA in air

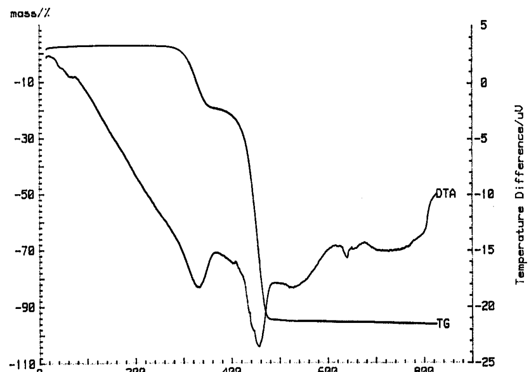


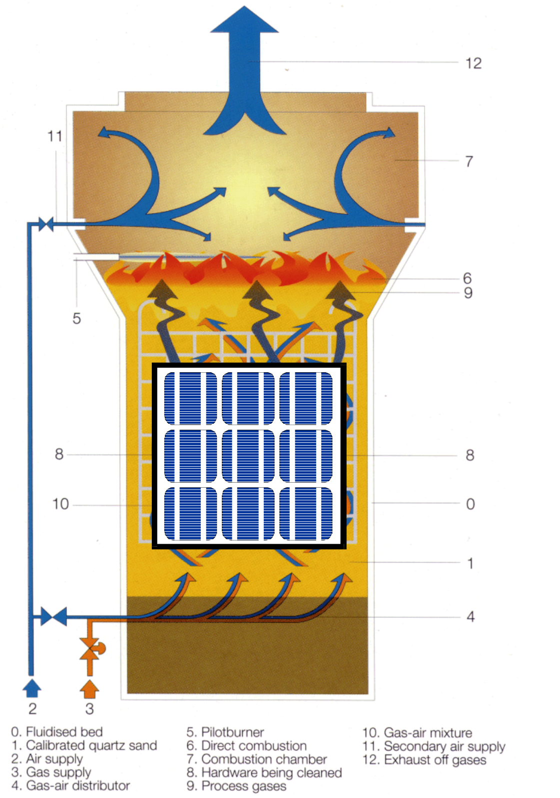
Figure 1b DTA/TG-curves from EVA in nitrogen

The EVA is burned away in the air atmosphere or decomposed under nitrogen at temperatures of 450°C resp. 480°C. The DTA/TG curves presented in fig. 1 shows this decomposition under ambient air or under nitrogen.

The tests with the thermal treatment under air resulted in a poor mechanical yield. This can be caused by the considerable temperature increase at the silicon surface due to the exothermic reaction leading to cracks.

Changing the furnace atmosphere from air to nitrogen avoids this exothermic reaction. With an optimised nitrogen flow and conveyor belt speed this reclaim process results in mechanical yields higher than 80%.

The most promising technique especially for industrial implementation is pyrolysis in a fluidised bed reactor [4].



The fluidised bed reactor (fig.2) is filled with very fine sand that has a narrow particle size distribution. Due to an optimised air stream this sand is in a hot boiling fluidised state. In this fluidised state the sand takes the physical properties of a liquid. The modules are loaded in a basket and immersed in the fluidised bed.

Gasification of the EVA and back side sheet of the modules, sustained by the mechanical action of the silica, takes place. The off gases emerge from the reactor surface and pass immediately through the flame shield serving simultaneously as postcombustion and as a heat source for the reactor. The even temperature profile throughout the bed, the perfect mixing and the intense contact with the reactor recovers the silicon wafers and the glass in the optimal conditions.

Different parameters have been investigated. The process temperature has been optimised around 450°C. At this temperature a process time of 45 min. seems to be optimal.

A very important parameter to optimise is the fluidisation velocity of the sand particles. This velocity is directly related to the average diameter of the particles. For the recycling of crystalline silicon modules the velocity is kept extremely low at 1 cm/sec with a particle diameter of 100 micron.

A better collection yield of the reclaimed wafers was obtained by putting each module in a netting envelope. Also the positioning of the module in the loading basket seemed to be very important. An angle of 60 degrees gives the best results but leads to a worse occupation of the useful surface and a decreased capacity. New fixing structures with vertical positioning are under study now and have already given satisfactory results.

All the tests done up to now are with prepared samples with different module encapsulation technologies. The tests started with small 8-cell modules and are gradually going to the 36-cells modules. The project target of 80% mechanical yield of the wafers is already obtained, but with the new fixing structures now under study better results are very likely. A yield of almost 100% is achieved for the glass sheets.

3. SILICON WAFER RECLAIM AND CELL REPROCESS OPTIMISATION

The reclaimed solar cells have very low efficiencies as they were heated to 450°C for at least 20 minutes. Screen printed cells are shunted after such a heat treatment and cannot be re-used as such but have to be cleaned, etched and reprocessed into new cells.

Lifetime mapping with an MFCA scan on cleaned monocrystalline wafers indicate a preservation of the material quality after the recycling process. On the contrary, even a higher lifetime was measured on reclaimed wafers from solar cells that had an aluminium back side metallisation. The high material quality of the silicon wafer is confirmed by the very good cell efficiencies after reprocessing.

A general cleaning and etching sequence of the metallisation for most of the reclaimed wafers was a 15% HF treatment followed by a H_2SO_4 : H_2O_2 4 to 1 solution at 80°C and finally followed by a 40% HNO_3 at 80°C. An emitter etch in 20% NaOH at 85°C is needed before starting the new cell process.

For reclaimed monocrystalline wafers the best process sequence is given in the following process flow chart.

Metal etching
I
Emitter and BSF etching
I
Surface texturisation
I
$POCl_3$ emitter diffusion
I
Parasitic junction removal
I
PE CVD SiN_X
I
Screen printing of metal contacts and cofiring

Despite a slightly worse texturisation almost the same results were obtained for reclaimed and for virgin wafers. Average results are presented in table 1.

	Jsc (mA/cm²)	Voc (mV)	FF (%)	Eff (%)
Reclaimed wafer	**34.8**	**618**	**76.1**	**16.4**
Virgin wafer	**34.9**	**617**	**75.8**	**16.3**

Table 1: Average illuminated IV parameters for reclaimed and virgin monocrystalline wafers.

The reprocessing of reclaimed multicrystalline wafers is somewhat more difficult. The emitter etch in 20% NaOH increases the step height at the grain boundaries, causing a lot of interruptions in the screen printed metallisation. The consequence is poor fill factors.

An optimised isotropic texturing process step overcame these problems. The PECVD SiNx process appeared again to be the best approach for reprocessing reclaimed wafers. The average cell results on reclaimed and virgin wafers are presented in table 2. Thanks to a better starting material the results for reclaim wafers were somewhat better.

	Jsc (mA/cm²)	Voc (mV)	FF (%)	Eff (%)
Reclaimed wafer	**33.6**	**618**	**76.6**	**15.9**
Virgin wafer	**32.9**	**611**	**76.1**	**15.3**

Table 2: Average illuminated IV parameters for reclaimed and virgin multicrystalline wafers.

Modules are made with these recycled wafers without any noticeable difference in mechanical yield. Accelerated ageing with the damp heat test does not show any additional degradation.

4. ECOLOGICAL IMPACT AND COST ANALYSIS

A life cycle analysis is made based on a module with 125 x 125 mm multicrystalline silicon cells. A standard module compared to a module using recycled wafers resulted in a 40% reduced energy consumption per generated kWh. The power generation is assumed in a sunny region for 20 years resulting in a total generation of 33 kWh/Wp or 71.9 kWh/waf. Table 3 shows the results.

	Consumed energy of PV module	
	Standard	**Recycled**
Silicon production	**7,55 kWh/wafer**	-
Solar cell production	**0,65 kWh/wafer**	**0,65 kWh/wafer**
Module production	**1,12 kWh/wafer**	**1,12 kWh/wafer**
Recycling at end of life	-	**0,4 kWh/wafer**
Total	**9,32 kWh/wafer** **0,129 kWh/kWh$_{Gen}$**	**2,17 kWh/wafer** **0,030 kWh/kWh$_{Gen}$**

Table 3: Energy content of a module using virgin wafers and a module using recycled wafers

The reuse of the recycled silicon wafer with high energy content for a second life time improves the energy pay back time considerably.

With the small additional energy consumption for the recycling, solar cell and module process we can generate again the same amount of energy namely 1,65 kWh/Wp for sunny regions and 0,86 kWh/Wp for continental regions.

Table 4 presents the calculations of the strongly reduced energy pay back time.

	Standard	**Recycled**
Energy input	**9,32 kWh/wafer or 4,26 kWh/Wp**	**2,17 kWh/wafer 0,99 kWh/Wp**
	Energy pay back time	
Sunny regions	**2,58 years**	**0,6 years**
Continental regions	**4,92 years**	**1.14 years**

Table 4: Energy pay back time for a module using virgin wafers and a module using recycled wafers

A second driving force behind the recycling process is the cost benefit. The high value of the silicon wafer is a significant cost benefit. The silicon wafer is recuperated in good condition and at relatively low cost. The cost calculations of the recycled silicon wafers are based on the presently available knowledge of the fluidised bed reactor process.

The following assumptions are made for this process:

- Mechanical yield of 80%
- Cycle time of 1 h gives capacity of 576 wafers/h
- Total investment cost of 575,000 Euro
  for a total line consisting of:
  fluidised bed reactor,
  a wet bench for etching and cleaning and
  a demi water installation.

The direct cost per recycled wafer as summarised in table 5, shows clearly the cost effectiveness of the process. The cost for the collection of the end of life modules is not included yet.

	Direct cost per recycled wafer
Investment	**0.047 Euro**
Energy	**0.011 Euro**
Etching, cleaning	**0.037 Euro**
Labour	**0.120 Euro**
Total	**0.215 Euro**

Table 5: Cost breakdown to recycle silicon wafers

5. CONCLUSIONS

Effective recycling processes were developed with very good results. The fluidised bed reactor process reached the industrial level by the construction of a pilot machine to demonstrate the exploitation capability.

The reclaimed silicon wafers preserved their initial high quality resulting in high efficiency recycled solar cells.

So, the PV industry has now a cost effective industrial recycling process available that can strengthen their positive image as clean energy producers.

6. ACKNOWLEDGEMENT

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