Recycling of Raw Materials, Silicon Wafers and Complete Solar Cells from Photovoltaic Modules

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Abstract: Photovoltaic modules (PVs) are an attractive way of generating electricity in reliable and maintenance-free systems with the use of solar energy. The average lifetime of photovoltaic modules is 25 to 30 years.

To offset the negative impact of photovoltaic modules on the environment, it is necessary to introduce a long-term strategy that includes a complete lifecycle of all system components from the production phase through installation and operation to disposal. Recycling of waste products and worn-out systems is an important element of this strategy.

Environmental benefits of recycling are related not only to the limited space of landfills, but also to energy saving, raw materials and emission reduction. An important argument for the recycling of photovoltaic modules is the reduction of energy consumption at their production stage through the reuse of existing purified materials.

The paper presents selected methods of recycling of used or destroyed PV modules and photovoltaic cells and the results of practical experiments.

Keywords: Recycling, photovoltaic modules, silicon, solar cells.

1. INTRODUCTION

Photovoltaic modules (PV) are an attractive way of generating electricity in reliable and maintenance-free systems using solar energy. The average lifetime of photovoltaic modules is 25 to 30 years. For many years there has been a worldwide increase in demand for photovoltaic modules. The cumulative power of photovoltaic installations in the world exceeds the impressive figure of 100 GW. Photovoltaic modules installed in 2013 set another record: more than 38.4 GW were newly installed worldwide and nearly 11 GW in Europe. In 2013, in addition to wind power, no other source of electricity has reached the level of newly installed capacity that photovoltaics have achieved in Europe. Some sources, such as gas, recorded negative values: more installations were closed than installed. This proves that photovoltaics has the potential to become an important part of the energy system, providing clean, safe and affordable energy throughout the world.

Scenarios for the development of photovoltaics predict that in the year 2017 only the installed power will reach 48 GW - 84 GW. This will mean that in 2017 the total output of PV installations in Europe will be between 124 and 180 GW [1]. Compound annual growth rate accounted for 44% of PV installations in the period from 2000 to 2013 [2]. The increasing use of photovoltaics (PVs) in the world's electricity production causes an increasing amount of waste in the form of worn or damaged cells and PV modules and there is a consequent need for more sustainable development projects. To offset PVs' negative effects on the environment, it is necessary to introduce a long-term strategy that includes a complete lifecycle of all system components from the production phase through installation and operation to disposal. Recycling of waste products and worn-out systems is an important element of this strategy.

The environmental benefits of recycling are related not only to the limited space in landfills, but also to energy saving and reduced emissions. Recycling of photovoltaic modules allows the recovery of many valuable materials, which saves energy and natural sources of raw materials. An important argument for the recycling of photovoltaic modules is the reduction of energy consumption at the production stage through the use of existing purified material.

The operational life of photovoltaic modules guaranteed by the manufacturer is 25 years, although there is a tendency to extend this period as the technology of their production improves. However, practice shows that many users exchange their PV installations before the theoretical end of life, after an average 17 years of use, in order to obtain better energy yields resulting from continuous technology improvements. At the stage of manufacture and assembly the level of waste is about 2 per cent. On the basis of the installed power in Europe and assumed life expectancy modules (17 years), the amount of

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photovoltaic waste is estimated to rise to 5,500,000 tons by 2026 [3]. From 14 August 2012 the second WEEE directive replaced the first WEEE directive and introduced many significant changes, including new levels of minimum electro waste collection from 2016. The new directive considerably broadens the scope of the provisions on electro wastes. From 2018 regulations will include all electrical and electronic equipment, classified in the six new open groups, including the category of large photovoltaic panels and the category of small equipment with integrated photovoltaic panels [4].

Photovoltaic technology is considered to be an energy source responsible for relatively small amounts of waste, as none is generated during the lifetime of PV modules, but we should not ignore the waste stream generated at the end of the exploitation phase of PV installations. A small stream of waste is also created at the production stage of products that are rejected by quality control, as well as during operation in the case of damaged modules, which show reduced efficiency (e.g. anti-reflective coating defects) [5]. The lifecycle of photovoltaic modules including recycling is shown in Figure **1**.

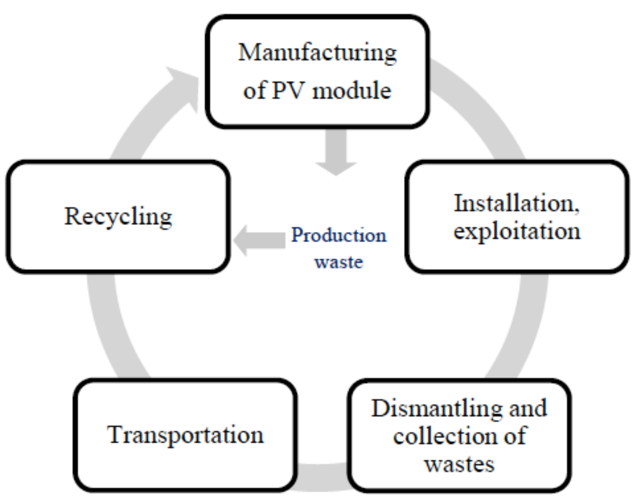

Figure 1: The lifecycle of photovoltaic modules including recycling.

2. CONTENTS OF PHOTOVOLTAIC WASTE AND LEGAL REGULATIONS

Photovoltaic modules may contain minor quantities of wastes, for which there are regulations, depending on the technology used: cadmium, lead, copper, nickel, selenium, silver [6]. Lead can be found:

- In solders (currently $Sn_{60}Pb_{40}$ with lead content below allowable standards which amounts to 0.1% by weight; some manufacturers use alloys that do not contain lead, e.g. $Sn_{96,5}$ $Ag_{3,5}$ - RWE Schott Solar) [7],
- In glass used to cover the modules (0-0.001% by weight); lead contained in glass is currently excluded from the EC directive 2002/95/EC [7],
- In the glaze contained in the paste for metallization used in the screen printing process,
- In the components of the inverters.

Cadmium is present only in CdTe and CIS with CdS cells (Cadmium EU Directive EU Directive 91/338 / EEC does not prohibit the use of modules of cadmium, because these modules occur in non-metallic form). In addition, in anti-inflammatory agents (older types) used in the housings of inverters and junction boxes bromine occurs. In the European Union production of polybrominated retardants such as pentaBDE and octaBDE has been forbidden since August 2004; however, decaBDE is not forbidden and penta-BDE is still used outside the European Union. It should be remembered that the modules for recycling come from different periods of production (since the eighties of the last century to the present). Good recovery of glass, steel, non-ferrous metals and semiconductor materials from photovoltaic installations is ongoing.

The aim of the challenges facing European organizations, as assessed by PV CYCLE, a non-profit organization dealing with the free collection and recycling of modules, is to achieve 85% recycling in 2020.

The flow of material in the recycling system modules is shown in Figure **2**.

3. PHOTOVOLTAIC CELLS BASED ON CRYSTALLINE SILICON

Currently, the dominant semiconductor material used for the production of photovoltaic cells is silicon in the form of mono- or polycrystalline tiles.

The observed silicon shortage and the growing global demand for photovoltaic modules have become the driving force for the development of thin-film photovoltaic technologies. As a result production of thin-film modules from amorphous silicon (a-Si), copper

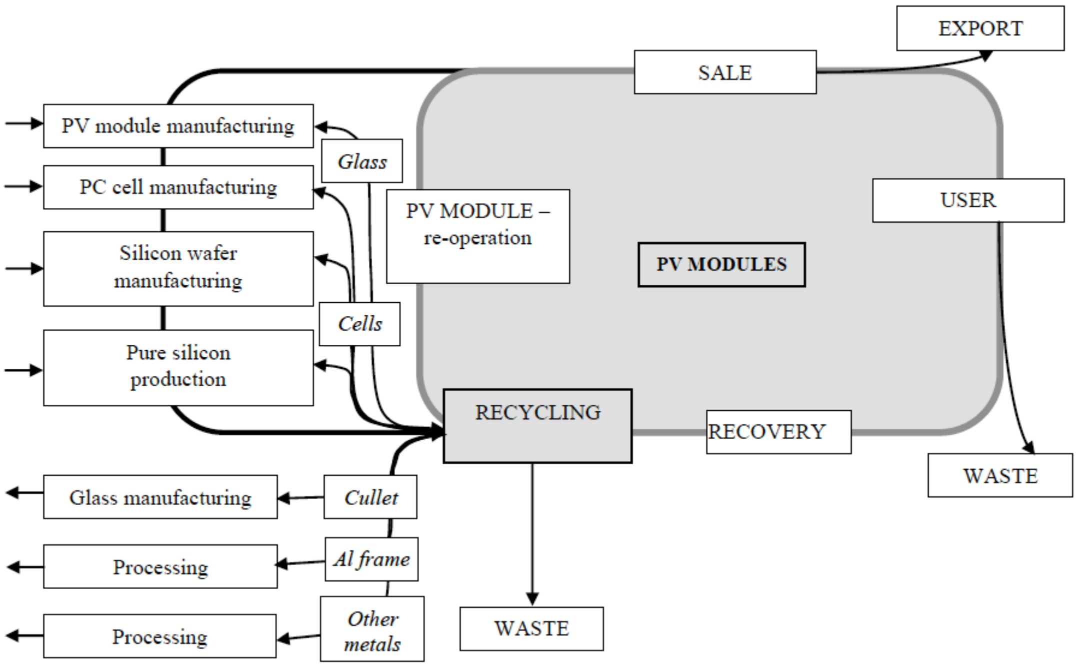

Figure 2: Material flow in the system of PV module recycling [8].

indium diselenide (CIGS) and cadmium telluride (CdTe) is steadily increasing. In this technology, often the entire module is made from a single cell. The advantage of thin-film technology is that it is committed to reducing the consumption of expensive materials, thus improving the ratio of price to power cell. Silicon technologies comprised 89% of the market, and thin-film technology the remaining 11% in 2012, according to the International Renewable Energy Agency [9].

It is possible to recover the silicon substrate as a whole and produce on its basis the PV cell of electrical parameters not worse than using a new material. If, for some reason, full recovery is impossible, the silicon can be reused in the production of new cells while worn, broken tiles can be melted down and reused in photovoltaic or electronics for the production of microprocessors and other integrated circuits and as an additive for steel, raising its quality.

In order to recover silicon as a 'wafer', suitable for use as a substrate in the production of new cells, the laminate layer (EVA poly (ethylene-co-vinyl acetate)) must first be removed from the module by thermal or chemical processes. Then, with a mixture of alkalis or acids, the anti-reflection layer, the metallization of the front and rear surface of cell and p-n junction have to be removed (Figure **3**). Optimization of chemical processes has been discussed in detail in [8], where the results of the use of optimized chemical processes and the outcome of verification by depositing new layers to produce a cell with parameters no worse than the originally presented.

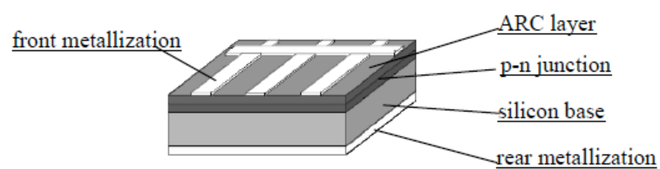

Figure 3: Scheme of crystalline silicon solar cell [10].

Figure **4** shows a flow diagram of the recycling of photovoltaic modules, leading to the production of new cells based on the recovered silicon substrate. Cell separation was performed by heating in a bed of silicon dioxide, SiO_2. Then individual layers of cells created in the course of manufacture (metallization, anti-reflective layer and p-n junction) were removed.

Metals removed by dissolution in 40% aqueous HNO_3 at 40°C were recovered from the solution by electrolysis, and 30% aqueous KOH solution was used to remove the metallization of the front. The best performance of the process was achieved at a temperature of 80°C.

The optimized mixture of 83.33ml HNO_3 (65%)/50ml HF (40%)/50ml CH_3COOH (99.5%)/1ml Br_2 was used to remove the AR coating film and p-n junction. Each step required rinsing with deionized water and drying.

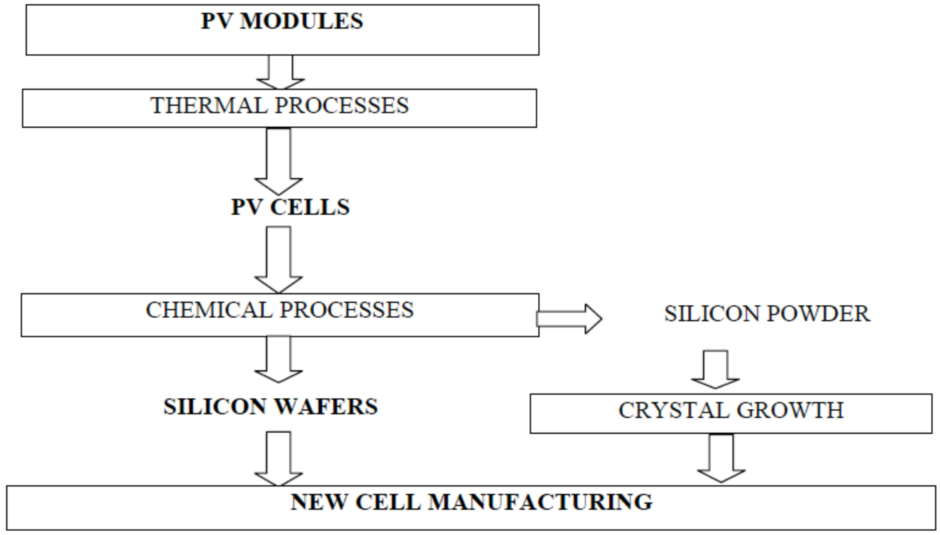

Figure 4: Process of recycling of photovoltaic modules - recovery of silicon wafers [11].

The process of recycling of photovoltaic modules and recovery of silicon wafers is presented in Figure **4**.

Optimal compositions of the mixtures and the design of technological lines for recycling of silicon photovoltaic cells have been registered in the Republic of Poland Patent Office under Patent No. 215 770 [12].

Recycling of one ton of silicon crystalline PVs allows for the reduction of about 800kg of CO_2 eq. and savings of 8.5 GJ of energy from non-renewable sources [13].

4. THIN-FILM SOLAR CELLS

The observed silicon shortage and the growing global demand for photovoltaic modules have become the driving force for the development of thin-film photovoltaic technologies. This has resulted in steadily increasing production of thin-film modules from amorphous silicon (a-Si), copper indium diselenide (CIGS) and cadmium telluride (CdTe).

In this technology, often the entire module is made from a single cell. The advantage of thin-film technology is the reduced consumption of expensive materials, thus improving the ratio of price to power cell.

The advantages of thin-layer cells are in particular: material saving and low price, saving on pure semiconductor materials, low loss of materials owed to avoidance of crystal growth and cutting of the monocrystalline block, integrated process of series connection of modules depending on the required voltage on the battery output, and possible simple realization of the cell stack, which allows for better utilization of the solar spectrum and thus increases the efficiency of conversion.

Amorphous silicon (a-Si), a non-crystalline allotrope derived from silicon, is massively used in the production of photovoltaic cells, LCD displays and OLED. The viability of the silicon in amorphous form is more than twice less than that of monocrystalline silicon and is equal to approximately 10 years. Production of photovoltaic cells from amorphous silicon differs significantly from technology based on crystalline silicon. In the vacuum chamber the gases are decomposed (SiH_4 or a mixture of SiH_4 with dopant gases such as PH_3 or B_2H_6) in a glow discharge and deposit a layer of amorphous silicon on the substrate. The technological processes of production of photovoltaic cells from a-Si are simple and save energy and material. In addition it is possible to obtain a cell with a large area. Unlike single crystal silicon technology, in this technology there are no material losses connected with cutting and polishing plates, which reduces the production cost of cells.

Cadmium telluride (CdTe) cells are produced on a glass substrate with a layer of transparent indium tin oxide (ITO) acting as the front contact, and then a very thin layer of n-type CdS and p-type CdTe act as the absorber. CdS absorbs small range of visible and blue light, allowing the rest of the spectrum to reach the active layer of cadmium telluride. The rear metal contact is produced by sputtering.

Cells manufactured from copper-indium selenide $CuInSe_2$ (CIS) and copper-indium-gallium-selenide $InGaSe_2$ (CIGS) are gaining in popularity. In cells of this type on glass substrate a metal layer is formed, creating ohmic contact with the absorber layer, the p-type semiconductor, which is the CIS or CIGS. An N-type semiconductor layer (cadmium sulphide CdS) that forms a p-n junction with this metal layer has the task of matching the edge of the conduction bands of the CIGS layer and the window, which is zinc oxide, ZnO. The substrate used for thin-film CIGS-type photovoltaic modules is soda lime glass or borosilicate. A molybdenum layer, which covers the soda-lime glass, forms a bottom contact.

In this type of cell cadmium occurs, which belongs to those elements with a very high degree of potential danger because of accumulation in the bodies of animals and humans. However, cadmium used in the photovoltaic industry is not dangerous because of the sealed housing of the module, necessary for long-term and stable operation. The low public awareness of its application remains problematic, despite the proven safety of its use with CdS and CdTe [14].

Depending on the type of thin-film module to be recycled, there are three ways of proceedings:

1. For CIGS modules, shredding with a stream of water and chemical treatment,

2. For CIGS and CdTe modules, thermal treatment (pyrolysis) and chemical treatment,

3. For modules based on a-Si, grinding and pneumatic separation of the polymer base [15].

Regardless of the type of photovoltaic module, there are three stages in the recycling process (Figure **5**).

The first step is delamination and then removal of the EVA laminate. In the final phase, the separation of the semiconductor material and the recovery of metals takes place [16].

The procedure for recovery of valuable materials from CIGS solar cells is as follows [18]:

- **Step 1:** manual removal and collection of metal frames and junction boxes with cables,

- **Step 2:** separating of the cover glass by heating module and mechanically separating the glass,

- **Step 3:** removal of residual EVA laminate from the surface by immersion in an aqueous based acetic acid,

- **Step 4:** mechanical separation of the CIGS absorber in the form of a metal powder,

- **Step 5:** separation of the soda-lime glass layer by dissolving molybdenum layer in dilute nitric acid.

In the case of CdTe modules, the procedure starts by grinding modules with various types of mills and crushers. Semiconductor films are removed by adding an acid in a slowly rotating drum made of stainless steel. The drum is emptied slowly into a classifier, where the glass is separated from the liquid. Glass is washed to remove residual semiconductor material. The solution is then passed through the column to remove copper and iron. Cadmium is recovered by electrolytic deposition, and tellurium by reactive precipitation. The metal-rich liquid is pumped into the precipitation and processed in three stages (in solutions with increasing pH). Then educts are concentrated. The filter cake produced from the slurry during the process is rich in metals, which in effect are recovered at 95% [19]. Freed semiconductor layers may also be removed from the crushed material by a wet process of grinding or flotation.

Comparative analyses of the gains which can be achieved during recycling of various types of solar cells and modules and the quantities of semiconductor material and glass recovered are presented in Table **1**.

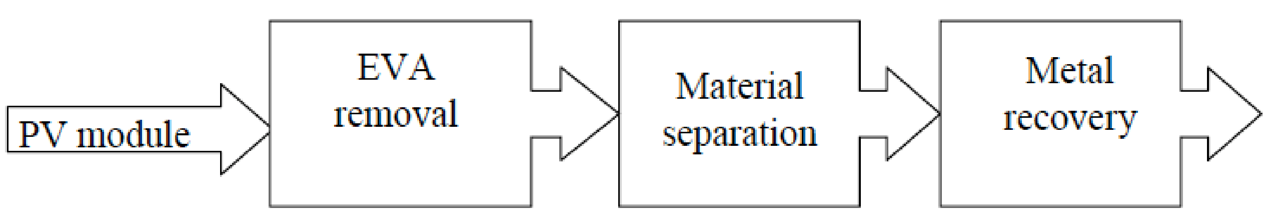

Figure 5: Recycling of thin-film photovoltaic module [17].

Table 1: Mass Recovery of Semiconductor Materials and Glass for 1m² of PV Module [20]

PV Cell Type	c-Si, mc-Si	a-Si	CIGS		CdTe	
			Ga	In	Cd	Te
Recovered semiconductor materials [g]	279.6	1.17	5.23	8.62	8.98	9.15
Recovered glass [kg]	16.64	N.A.	17.680		16.64	

To sum up: the recycling of the most valuable materials can be performed at the production stage in the case of cells and modules that do not meet quality requirements, as well as in the case of modules worn or damaged as a result of inadequate transport conditions, improper installation or misuse. Recycling can reduce the overall environmental impact of the product lifecycle in the category of impact: acidification, global warming, resource consumption.

To achieve environmental benefits, the environmental impact of the recycling process must be smaller than the environmental impact of the material production process and, although the cost of storage module landfill is smaller, recycling must be economically viable [21].

The results of a lifecycle analysis (LCA) in terms of cumulative energy demand (CED), global warming potential (GWP) and acidification potential (AP) per square metre of a CdTe PV module are as follows: CED 84.7 MJ, GWP 4.53kg CO_2 eq., 8.58 g, AP SO_2 eq. [22]. This confirms that recycling PV modules is justified not only economically, but also environmentally.

It needs to be highlighted, that further studies are needed to optimize the recycling process of CdTe modules which are based on recycling of glass, cadmium and tellurium and minimizing energy consumption and emissions throughout the lifecycle [23].

CONCLUSION

Recycling helps in reducing the consumption of valuable raw materials, production costs and environmental protection. An important argument for the recycling of photovoltaic modules is the reduced energy consumption at the production stage through the use of existing purified material.

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