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CURRENT TRENDS IN RECYCLING OF PHOTOVOLTAIC SOLAR CELLS AND MODULES WASTE

RECYKLING ZUŻYTYCH OGNIW I MODUŁÓW FOTOWOLTAICZNYCH - STAN OBECNY

Abstract: In comparison to other energy producing techniques, photovoltaics (PV) is one of the most promising options: no emission of any matter into the environment during operation; extremely long operation period (estimated average: 25 years), minimum maintenance, robust technique, aesthetic aspects. The use of photovoltaics is rapidly increasing, and the respective market is developing accordingly. Although PV manufacturing equipment is now excluded from the scope of RoHS, according to the Kyoto Protocol and the EU Directives WEEE and RoHS the use of hazardous substances in electric/electronic devices has to be reduced stepwise to approximately zero level. Furthermore, a total recycling of nearly all materials involved is aimed. Thus, major attention is directed to avoidance of environmental pollution through combustion or landfill, to regain valuable material, to promote the development and use of renewable energy sources. As the lifetime of PV cells themselves is much longer than that of PV modules and the manufacturing process of cells requires much energy consumption, the reuse of base material of the cells is economically justified. The aim of this work was to develop and evaluate existing methods of PV cells and modules recycling. The article discusses the main outcomes and analyses the significance of recycling in relation to the environmental profile of the production and total life cycle of photovoltaic cells and modules.

Keywords: recycling, photovoltaic cells, photovoltaic modules, waste, renewable energy sources

PV technology is considered as an energy source that has very minimal waste because there is none produced during operation but there is still waste that cannot be ignored that is created by the decommissioning of the solar modules at the end of their lives.

Typical defects limiting the long lifetime of some modules include broken glass, laminate defect and electrical defects. Further reasons for solar module recycling should be poor efficiency and an unacceptable appearance (*eg* poor quality anti-reflective coating).

In response to the growing problem of excessive waste, several countries adopted liability schemes in which manufacturers must take responsibility for their products in attempts to slow the filling of landfills and the consequential releases of toxic materials

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from the discarded products. According to the Kyoto Protocol and the EU Directives WEEE [1] and RoHS [2] the use of hazardous substances in electric/electronic devices has to be reduced stepwise to approximately zero level, simultaneously directives should not prevent the development of renewable energy technologies that have no negative impact on health and the environment and that are sustainable and economically viable. Extended Producer Responsibility is becoming an increasingly popular solution to the problems of electronic wastes. Responsibility laws across the country are demanding manufacturers of these products to take responsibility for their reuse, recycling, and disposal.

Recovering pure materials from damaged or end-of-life PV modules is environmentally beneficial because its positive impact is greater than the environmental burdens of recycling. The energy consumption, the water and chemical consumptions and the transportation cost should be taken into account.

Photovoltaic modules may contain small amounts of regulated materials such as cadmium, tellurium, lead and selenium, which vary from one technology to another. Environmental regulations can determine the cost and complexity of dealing with end-of-life PV modules. If they were classified as hazardous, then special requirements for material handling, disposal, record keeping and reporting would escalate the cost of module decommissioning.

For Europe, the emergence of end-of-life modules in 2040 is estimated to rise to 33 500 Mg (tons) [3]. The regional distribution of waste generated varies greatly. Waste generated in Germany accounts for 80% in 2008 and 50% in 2020. The disposal of PV systems will become a problem in view of the continually increasing production of PV modules. These can be recycled for about the same cost as their disposal.

Currently, two basically different converter materials of photovoltaic (PV) modules are in use, namely semiconductor silicon (to a greater extent) and thin-film compound semiconductors like CIS (*copper indium selenide*) and CdTe (*cadmium telluride*).

Silicon is separated into multiple categories according to crystallinity and crystal size in the resulting ingot, ribbon, or wafer:

1. *monocrystalline silicon* (c-Si): single-crystal wafer cells tend to be expensive, and because they are cut from cylindrical ingots, do not completely cover a square solar cell module without a substantial waste of refined silicon. Hence most c-Si panels have uncovered gaps at the four corners of the cells;
2. *multicrystalline silicon* (poly-Si or mc-Si): made from cast square ingots - large blocks of molten silicon carefully cooled and solidified. Poly-Si cells are less expensive to produce than single crystal silicon cells, but are less efficient;
3. *ribbon silicon* is a multicrystalline silicon formed by drawing flat thin films from molten silicon; these cells have lower efficiencies than poly-Si, but save on production costs due to a great reduction in silicon waste, as this approach does not require sawing from ingots [4].

Copper indium gallium (di)selenide (CIGS) is a I-III-VI_2 compound semiconductor material composed of copper, indium, gallium, and selenium. The material is a solid solution of *copper indium selenide* (CIS) and *copper gallium selenide*, with a chemical formula of $CuIn_xGa_{(1-x)}Se_2$, where the value of x can vary from 1 (pure copper indium selenide) to 0 (pure copper gallium selenide). It is used as light absorber material for thin-film solar cells [5].

A cadmium telluride solar cell uses a cadmium telluride (CdTe) thin film, a semiconductor layer to absorb and convert sunlight into electricity. The cadmium present in the cells would be toxic if released. However, release is impossible during normal operation of the cells and is unlikely during fires in residential roofs. A square meter of CdTe contains approximately the same amount of Cd as a single C cell nickel-cadmium battery, in a more stable and less soluble form [6].

Crystalline silicon modules represent 85÷90% of the global annual market today. C-Si modules are classified into two main categories: *single crystalline* (c-Si) and *multi-crystalline* (mc-Si). Thin films currently account for 10 to 15% of global PV module sales (Table 1).

Table 1

Market share of different photovoltaic technologies (on the base of: [7, 8])

Technology	Market share
c-Si	44%
mc-Si	45%
Ribbon	2.30%
a-Si	4.70%
CIS, CIGS	1.20%
CdTe	2.70%

Recycling technologies

Photovoltaic modules in crystalline silicon solar cells are made from the following elements, in order of mass: glass, aluminium frame, EVA copolymer transparent hermetizing layer, photovoltaic cells, installation box, Tedlar® protective foil and assembly bolts. The procedure for recovering valuable constituent materials from monocrystalline, polycrystalline and thin film modules is as follows: removing and collecting the metal frame, junction box and cable; separating the cover glass; removing the EVA from the surface of devices; chemical treatment of the parts.

The typical composition of CIS thin-film solar modules is as follows: glass (84%), aluminium frame (12%), the polymer encapsulant (3%, *eg* EVA). The most essential materials forming the photovoltaic layers (Mo, Cu, In, Ga, Se, Cd, Zn, S) are only a very small fraction of about 23 grams in a 15 kg square meter sized module.

CdTe PV modules are composed of four layers: a transparent conducting oxide layer consisting of SnO_2 - a front contact on glass substrate, a cadmium sulphide (CdS) - a *n*-type layer, CdTe film - an absorber layer and a back contact consisting of a copper layer. Research on the recycling of CdTe PV modules and manufacturing waste aims to optimize the separation and recovery of glass, cadmium and tellurium while minimizing life-cycle emissions and energy use, under the constraint of low cost.

The major tasks of the process are: removal of glass from the metals and the recycling of glass, separation of Te from Cd and other metals and recovery of Te because of its intrinsic value, recovery of Cd for reuse or effective sequestration [9].

Table 2 presents the short description of recycling process for these two main groups of photovoltaic solar cells and modules: crystalline and thin film.

Table 2

Recycling processes for different solar cells

Type of the technology	Solar cell production technology	Recycling process
Crystalline	c-Si mc-Si	Two steps of the process: the first one is pyrolysis, which recovers crystalline silicon wafers from the modules. In this process the *ethylene vinyl acetate* (EVA) lamination layer is vaporized by the inert atmosphere pyrolysis at about 500ºC; the second step is chemical etching: removal of metal coatings, *antireflective coatings* (ARC) and diffusion layers; common acidic chemical etching mixtures are based on $HF\text{-}HNO_3\text{-}H_2O$ solutions; the etching recipes have to be adapted to the different cell technologies; the chemical etching of semiconductors with this mixture is divided into two steps - oxidation and reduction - followed by dissolution of the oxidation products to form a soluble ion complex.
Thin film	a-Si	Currently no literature explaining the recycling process of amorphous silicon solar cells [10].
	CIGS	A smeltering process or acid baths to recover the metals, including selenium (Se), indium (In) and gallium (Ga); the glass is processed through thermal decomposition, solvent or acid dissolution to remove any remaining PV layers and is recovered [11].
	CdTe	CdTe thin film modules are recycled using a combination of mechanical and chemical process steps; chemical stripping of the metals and EVA and successive steps of electrodeposition, precipitation and evaporation to separate and recover the metals cadmium and tellurium; the EVA is skimmed from the chemical solution for potential reuse and the glass and frame are recovered [12].

The recovery of semiconductor material from solar cells and wafers involves complicated and technically complex steps and exhibits the least favourable ecological balance. The diversity of the starting material means that the classification of material according to quality is very important. Semiconductor materials being considered for reuse are: silicon (Si), indium (In), gallium (Ga), cadmium (Cd), tellurium (Te), cadmium sulfide (CdS).

The comparative analysis for the profit of recycling process for different type solar cells determines the amount of the semiconductor material and glass - the obtained results are presented in the Table 3.

Table 3

The mass of recovered semiconductor material and glass for the assumed area of 1 m^2 module [10]

Type of PV cells	c-Si, mc-Si	a-Si	CIGS		CdTe	
			Ga	In	Cd	Te
Mass of recovered semiconductor materials [g]	279.6	1.17	5.23	8.62	8.98	9.15
Mass of recovered glass [kg]	16.64	n.a.	17.680		16.64	

Recovering pure silicon from damaged or end-of-life PV modules is environmentally beneficial because its positive impact is greater than the environmental burdens of recycling. The energy consumption, the water and chemical consumptions and the transportation cost should be taken into account. The energy payback time could be decreased from 2.5 years in sunny regions and 4.3 years in continental regions [13] in the case of standard modules to 0.6 years in sunny regions and 1.14 years in continental regions in the case of recycled modules [14].

Some solar manufacturing companies have begun to voluntarily recycle solar modules, but such initiatives may be driven by environmental responsibility rather than economic benefit.

The RESOLVED project (EU-LIFE program RESOLVED, LIFE04 ENV/D/000047) aims to demonstrate sustainable recycling strategies for photovoltaic thin film modules (CdTe and CIS) based on wet mechanical processes to reduce the amount of chemicals used for conventional recycling and the amount of waste. The main steps in both strategies are: destruction of the laminate, separation of the semiconductor from the glass substrate, enrichment of the semiconductor material, reuse of the recycled semiconductor for the production of thin film modules.

Complete PV modules can be dismantled thermally. Investigations on thermal dismantling were carried out with pieces of modules in a lab-scale furnace. Due to heat impact, the module composite was divided into a carrier glass and a protection glass. The carrier glass is coated with the thin film, the semiconductor materials, which were removed in the following step. The protection glass can enter the glass recycling process without further treatment. The separation of the semiconductor layer can be done by blasting. The broken modules were treated mechanically by crushing and milling in order to grain size reduction and to uncover the semiconductor layer. The liberated semiconductor layers were removed in a wet mechanical attrition process using frictional forces. The preconcentration of the CIS- and CdTe-fines was done by wet mechanical processes like flotation. The CdTe flotation products were purified to semiconductor grade material and can be used for the production of new modules [15].

Currently only two processes in the market are operated in an industrial scale. Since June 2003 Deutsche Solar AG is operating a recycling plant for modules with crystalline solar silicon cells. The aim of the process is to recover the silicon wafers so that they can be reprocessed and integrated in modules again. Although the energy consumption during the recycling process is essential, the use of recycled wafers for wafer production instead of new ones can halve the Energy Payback Time (EPBT) of a module. Due to the reuse of recovered wafers and the recycling of glass and metals the recycling process of Deutsche Solar AG leads to a decrease of environmental burden by avoidance of the production of new wafers and material like glass [16].

First Solar is the first PV company to implement an unconditional prefunded Collection and Recycling Program for damaged and end-of-life modules. As part of its commitment to environmental excellence and in line with the concept of extended producer responsibility, First Solar's Module Collection and Recycling Program is designed to: provide collection and recycling free of charge to First Solar module owners, achieve a high recycling rate of valuable materials for use in new solar modules or other new products, improve the overall environmental profile associated with PV module production. The recycling includes the following process steps:

- Particle size reduction using a shredder to break the glass into large pieces and a hammer mill to crush the broken glass into 4-5 mm pieces.

- Semiconductor film removal in a slowly rotating leach drum using sulphuric acid and hydrogen peroxide.
- Solid-liquid separation by emptying the content of the leach drum into a classifier where glass is separated from the liquids.
- Glass-laminate material separation by means of a vibrating screen where the glass is separated from the larger pieces of Ethylene Vinyl Acetate (EVA).
- Glass rinsing to remove any residual semiconductor material that physically remains on the glass.
- Precipitation of the separated metal components using sodium hydroxide and concentration in a thickening tank; the resulting filter cake is packaged for metals recovery by a third party.

First Solar‘s module recycling process is designed to recycle up to: approximately 95% of semiconductor material for use in new modules, approximately 90% of glass for use in new glass products [17].

Conclusions

Photovoltaic panels contain material which can be recovered and reused once their modules reach the end of their life cycle. Industrial processes to recycle both crystalline silicon cells and thin-film modules are already established, and can retrieve substances like glass and aluminum, as well as semiconductor materials such as silicon, copper, indium, cadmium and tellurium.

Photovoltaic module waste is expected at two levels: in-plant generated manufacturing waste and end of-life module waste. An efficient module recycling method can reduce the environmental impacts of manufacturing waste as well as end-of life module waste and recover the materials for future use.

To obtain an environmental benefit, the impact related to the recycling process has to be lower than that related to the production of the replaced semiconductor material. Although the cost of landfill disposal of solar modules is lower than the cost of recycling the modules, recycling is environmentally profitable.

It must be encouraged that in future the design and production of PV components facilitates the end-of-life dismantling of components into the parts that can be reused or recycled.

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RECYKLING ZUŻYTYCH OGNIW I MODUŁÓW FOTOWOLTAICZNYCH - STAN OBECNY

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Abstrakt: W porównaniu do innych metod produkcji energii, technologia fotowoltaiczna jest jedną z najbardziej obiecujących opcji: brak emisji z substancji do środowiska podczas pracy, bardzo długi okres eksploatacji (szacowany średnio na 25 lat), minimalna konieczność konserwacji, solidna technika, atuty estetyczne. Rynek modułów fotowoltaicznych na świecie rozwija się intensywnie, a stale rosnący udział modułów fotowoltaicznych (PV) w światowej produkcji energii elektrycznej powoduje, iż zwiększająca się ilość odpadów - w postaci zużytych lub uszkodzonych ogniw i modułów PV - spowoduje w najbliższych latach konieczność bardziej racjonalnego ich zagospodarowania. Aby moduły fotowoltaiczne pozostały bez negatywnego wpływu na środowisko, konieczne jest wprowadzenie długofalowej strategii obejmującej kompletny „cykl życia" wszystkich elementów systemu: od fazy produkcji, poprzez montaż i eksploatację aż do utylizacji. Recykling odpadów produkcyjnych i zużytych systemów jest istotnym elementem tej strategii. Korzyści środowiskowe recyklingu są związane nie tylko z ograniczeniem miejsca na składowiskach odpadów, ale również z oszczędnością energii, surowców i ograniczeniem emisji. Celem pracy było przedstawienie i ocena istniejących metod recyklingu ogniw i modułów fotowoltaicznych oraz wpływu tego procesu na środowisko naturalne.

Słowa kluczowe: recykling, ogniwa fotowoltaiczne, moduły fotowoltaiczne, zagospodarowanie odpadów, odnawialne źródła energii